THE UNIVERSITY OF ALBERTA

PARTIAL OXIDATION OF BUTANE

II   The Homogeneous Gas Phase Reaction

Influence of Pressure, Composition and Reaction Time

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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by

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TABLE OF CONTENTS

TABLE OF CONTENTS Continued

TABLE OF CONTENTS Continued

APPENDIX

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LIST OF ILLUSTRATIONS

LIST OF GRAPHS

iv

LIST OF GRAPHS continued

LIST OF TABLES

THE PROBLEM

The partial oxidation of butane has been
selected by the Research Council of Alberta as one of
a series of long term basic research projects in the field
of natural gas utilization. This phase of the project was
largely exploratory with an objective of recording the
effects of pressure, composition and reaction time upon
the reaction for a fixed reaction-initiating temperature.
Recognition of the salient features of the reaction and
the influences of the process equipment design were also
stressed.

ABSTRACT

The homogeneous gas-phase reaction of normal butane with oxygen was performed in a single-pass reactor of fixed length, immersed in a bath which boiled substantially constant at 725°F. Useful products identified included methanol, ethanol, acetaldehyde, acetone and formic acid. The effects of pressure, composition and reaction time are presented in the following table:

Parameter	Pressure	Reaction Time	Nitrogen	Butane	Oxygen
Pressure (psia)	variable	100	100	100	100
Reaction time (sec.)	3.0	variable	3.0	3.0	3.0
% Butane	3.0	3.0	1:1	variable	3.0
% Oxygen	3.0	3.0	ratio	3.0	variable
Range tested	50-175	0.8-4.5	1.5-6.0 butane	1.5-6.0	1.5-6.0
Limiting value	50	1.0	1.5 butane	none	1.5
Optimum range	115-135	1.0-2.0	3.5-4.5 butane	3.0-4.5	3.5-5.0

Optimum conversion to useful products was of the order of 10 per cent of the total carbon introduced with the exception of the runs where the butane to oxygen ratio was constant but their concentration was changed. In this case, a carbon conversion of 22 per cent was indicated. Evidence of a chain reaction is indicated by an observed reaction induction period of approximately 0.70 sec. and perhaps, by a minimum oxygen concentration critical to reaction propagation.

The thermal history of the reaction was deduced from five temperatures taken at equal intervals along the reactor, heats of reaction obtained from enthalpy balances and overall heat transfer coefficients for the reactor. The course of the reaction was similar to a "run-away" type where the reaction rate increases exponentially because of inability to dissipate quickly the heat liberated. The reaction proceeded over a period of 1.0 sec. after which only cooling of the hot gases was evident.

Overall heat transfer coefficients for the reactor were based on data obtained in tests where air was both heated and cooled by the bath. Gas film coefficients were estimated from other published correlations and from these values, the bath film coefficients were calculated. Neither film was indicated to be controlling and at the lower flow rates, the gas flow may overlap into the transitional flow region.

INTRODUCTION

The term "petrochemical" is today generally applied to those industrially important chemicals which use natural gas or petroleum hydrocarbons as their basic raw material. The majority of "petrochemical" processes based on natural gas may be classified according to the following general approaches:

1. Synthesis from "reformed" natural gas

The chemical may be synthesized from the gases carbon monoxide and hydrogen obtained when methane is treated with steam and oxygen at high temperatures in the presence of catalysts.

2. Oxidation

The hydrocarbons are oxidized directly to useful oxygenated organic derivatives.

3. Pyrolysis

The hydrocarbon is decomposed to other forms primarily olefins by heating at high temperatures.

4. Substitution

These include the other processes whereby hydrocarbons under special conditions are made to undergo halogenation, nitration, sulfonation, Friedel-Crafts and other reactions.

While oxygenated organic chemicals may be obtained from hydrocarbons treated from any of these approaches, the present

discussion is limited to the direct oxidation of gaseous paraffins.
This oxidation may be performed with air, oxygen or chemical oxidizing
agents. Methane, ethane, propane and butane constitute the bulk of
the feed material and their oxidation products include alcohols,
aldehydes, ketones, acids, esters and alkyl oxides as well as carbon
dioxide, carbon monoxide and water. In commercial oxidations, air
is usually preferred as the oxidizing medium.

Several technical obstacles arise in direct oxidation
processes. The process must be carried out with non-inflammable
mixtures and so, either air or hydrocarbon must be in considerable
excess, the latter being preferable. Excess air greatly limits the
hydrocarbon concentration and under these conditions, complete
oxidation of the hydrocarbons would be promoted. Air also reduces the
product concentration in the exit gases and results in increased
recovery costs. With excess paraffin, only low conversion per pass
is attained necessitating recovery and recycling of the excess hydro-
carbon. The process yields mixtures of products which require expensive
separational methods. The overall process yields of useful products
are not high owing to the loss of carbon as carbon monoxide and carbon
dioxide.

Early development of these processes was delayed by the
difficulty in controlling the reaction to prevent complete combustion.
of the hydrocarbons to carbon dioxide and water. With decreasing
chain length in the aliphatic paraffins, the conditions needed to
initiate the reaction become increasingly more severe. This is

particularly noted with methane and ethane where most of the reaction
intermediates are more easily oxidized than the original reactant.
To control the reaction and obtain yields of intermediate oxygenated com-
pounds, the following methods were employed:

1. Use of low oxygen-hydrocarbon ratios in feed stock.

2. Use of short reaction times followed by an
    instantaneous quench.

3. Use of catalysts and higher pressures to reduce
    the initiation temperature.

4. Use of inert gases to reduce concentrations of re-
    actants and to absorb the heat of reaction.

Commercial processes involving direct oxidation of the
lower paraffins were pioneered by the Cities Service Oil Company
in 1926, at Tallant, Oklahoma. According to this company's patents (8),
the feed is comprised of methane, ethane, propane and butane mixed
with about 10 percent by volume of air. The reaction at 860°F and
20 atm. over a contact catalyst yielded methanol, formaldehyde,
acetaldehyde and lesser quantities of acetone and dimethyl acetal.
Oxygen is consumed completely and after product recovery, the un-
reacted hydrocarbons with necessary makeup are recycled. Reaction
time is of the order of a few seconds. At 20 atm. the formaldehyde
yield is at its maximum but at 50 atm., methanol is the main product.

More recently, the Celanese Corporation of America has
successfully operated plants near Bishop, Texas. Using direct
oxidation of propane and butane, the products formaldehyde, acetalde-

hyde, propionaldehyde, acetone, methyl ethyl ketone, methyl,
ethyl and n-propyl alcohols, formic, acetic and proprionic acids,
and tetrahydrofuran are obtained. One of their patents (7) claims
control of secondary reactions by very rapid reaction in the presence
of large volumes of inert gas which limit the temperature rise. An
illustration is given in which one volume of butane is mixed with
110 volumes of steam and 10 volumes of air. The reaction is performed
at 20-30 atm. with a maximum reaction time of 1.15 sec. The butane
is preheated to 302°F and the steam-air mixture is preheated to 752°F.
The principle of limited oxidation per pass and recycling of unreacted
hydrocarbons together with air and hydrocarbon makeup is employed.
At Edmonton, Alberta, Canadian Chemicals Limited has undertaken the
construction of another large petrochemical plant based upon the
Celanese oxidation process. At this date, plant operation has not
commenced so that no operating details are available.

The scant information released by companies successfully
employing direct oxidation processes is not of much value in clarifying
the basic aspects of hydrocarbon oxidation. Much discussion of the
process problems is published (14, 30, 33) but significantly it too
is qualitative.

The field of direct hydrocarbon oxidation provides another
example where successful application and technology have out-distanced
the advancement of the underlying theoretical concepts. Much more
fundamental data on hydrocarbon oxidation, particularly of the higher
aliphatics, are required.

LITERATURE REVIEW OF THEORETICAL WORK

ON HYDROCARBON OXIDATION

The production of organic compounds by direct oxidation
of paraffins with air or oxygen has been the subject of much
investigation. The correlation of this work has been extremely
difficult because minor changes in operating conditions and the
presence of catalytic materials directly affect the extent and
nature of the reaction. Fundamental work other than from recent
publications, as summarized in this section, is selected mainly
from several reviews by Goldstein (17), Brooks (5), Egloff, Nordman
and Van Arsdell (12) and Linford (20).

Theories of Hydrocarbon Oxidation

Before entering the discussion of the experimental results
obtained by workers in this field, an insight into proposed mechanisms
of oxygen attack on paraffins should be of value. Three basic theories
have been suggested but widespread acceptance of a single theory is
not manifest. Indeed, much good experimental evidence may be cited
to support each of the assumed mechanisms.

1. Hydroxylation Theory

The oldest mechanism, the hydroxylation theory, was developed
mainly by Bone and co-workers (3a) who proposed a series of hydroxylations

and thermal decompositions. This theory indicates alcohols would

$$CH_4 \xrightarrow{\ O\ } CH_3OH \xrightarrow{\ O\ } CH_2(OH)_2 \xrightarrow{\ O\ } CH(OH)_3 \searrow$$
$$\qquad\qquad\qquad\qquad\qquad \downarrow \qquad\qquad\qquad\qquad \downarrow \qquad\qquad\quad CO_2$$
$$\qquad\qquad\qquad\qquad CH_2O \qquad\qquad\qquad CO \nearrow$$
$$\qquad\qquad\qquad\qquad \downarrow O$$
$$\qquad\qquad\qquad\qquad HCOOH$$
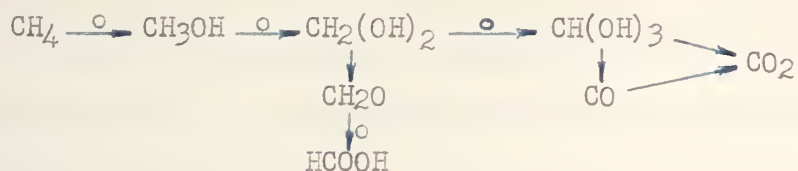
be the primary products and where the reaction has been stopped in
its initial stages, methane oxidation at ordinary pressures has
revealed the presence of methanol in considerable quantities. For
the higher paraffins having initial oxidation temperatures lower
than those of the alcohols, alcohols are frequently noted in the
oxidation products. Under some conditions, propane and butane
appear to be oxidized directly to aldehydes by oxidation of the
carbon atom at the end of the carbon chain. Primary alcohols have
also been converted to aldehydes by direct dehydrogenation. It has
been pointed out that Bone's theory would require splitting of the
oxygen molecule which is considered unlikely at the temperatures
employed.

2. Peroxide Theory

The peroxide theory as first enunciated by Bach (1) and by
Engler and Wild (13) proposed that peroxides or alkyl hydrogen peroxides
are the initial products in hydrocarbon oxidation. These unstable
alkyl peroxides decompose to aldehydes, acids, water and carbon dioxide.

$$CH_4 + O_2 \longrightarrow CH_3OOH \longrightarrow HCHO + H_2O$$
$$\qquad\qquad\qquad\qquad \downarrow CH_4$$
$$\qquad\qquad\qquad\qquad 2CH_3OH$$
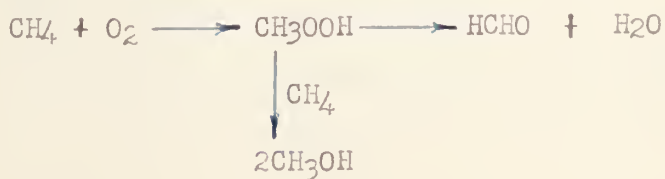
This theory avoided the atomic oxygen mechanism inherent in the hydroxylation theory because the peroxides could be formed by direct combination with molecular oxygen. In oxidations of hexane, heptane and octane with air in a flow system at $620^{\circ}F$ both peroxides and aldehydes have been detected. One rather vague criticism is raised because aldehydes are considered normal products from alkyl peroxide decompositions and yet both of these products are found in association.

Both hydroxylation and peroxide reactions are said to be initiated in chain reaction series to account for the observed inhibition of hydrocarbon oxidation by surfaces. The proposed chain starting and chain ending mechanisms are numerous.

3. Atomic Chain Theory

The atomic chain theory was proposed by Norrish (23) who considered the formation of a hydrocarbon radical and an oxygen atom. The chain initiating oxygen is formed, in the case of methane, from formaldehyde produced in a surface reaction and its subsequent oxidation to formic acid with the liberation of an oxygen atom. The oxygen atom may initiate the chain reaction, which may repeat or the chain be broken.

$$O + CH_4 \longrightarrow : CH_2 + H_2O \xrightarrow{O_2} CH_2O + O$$

To terminate the chain, a surface reaction or a ternary collision may occur

$$CH_4 + O + X \longrightarrow CH_3OH + X^*$$

where X is an inactive or inert molecule. This theory differs from the

peroxide theory in that the reaction is propagated by atoms and
radicals and not by an energy chain mechanism.

In the above examples, the proposed mechanisms are illustrated
by attacks upon a methane molecule. It is possible that the interpretation
of the reaction of butane with oxygen may be oversimplified but the
mechanisms illustrated should be basic to attacks upon any hydrocarbon.

Other investigators including Lewis (19), von Elbe and
Lewis (28), Edgerton (11) and Bludworth (3) have modified the above
mechanistic concepts but to date no single theory satisfactorily
explains all phenomena associated with hydrocarbon oxidation. More
recently, the conjectures are raised that more than one mechanism may
be involved or that some oxidations are isolated problems.

Thermal Oxidation of Alkanes

The greater part of development work has been directed
towards the oxidation of the hydrocarbons, methane, ethane, propane
and butanes. Some general rules applicable to oxidation have been
formulated (12) regarding the hydrocarbon structures and their
relation to ease of oxidation.

1. The longer the straight chain of carbon atoms, the
   easier is their oxidation.

2. Branching in the molecule increases the difficulty
   of oxidation.

3. The thermal stability of pure normal paraffins is
   inversely proportional to chain length.

4. The initial combustion temperature is lowered as

the carbon content of the normal paraffins increases.
Nearly all of the possible oxidation products, alcohols, aldehydes,
ketones, acids and oxides, have been obtained. Chain rupture of the
higher hydrocarbons always occurs so that oxygenated molecules with
the same number of carbon atoms as the hydrocarbon constitute only a
small fraction of the useful products. Use of catalysts in oxidation
of the simpler paraffins tends to increase the rate and reduce the
yields of intermediates.

1. Methane

Methane at atmospheric pressure is not oxidized appreciably
below 1110°F according to Blair and Wheeler (2). All intermediates
are susceptible to oxidation at temperatures below that of methane.
Wiezevich and Frolich (32) found nearly pure methane required at least
970°F for oxidation at pressures of 130-135 atm. Introduction of ethane
in increasing amounts decreased the initiation temperature further and
also increased methanol yields to the extent that some methane oxidation
was necessary to account for all of the reacted carbon. Low pressures
favoured formaldehyde yields at the expense of methanol whereas higher
pressures reversed this trend. Burke and Fryling (6) oxidized methane
with 50 per cent air at temperatures of 390° to 930°F and pressures of
200-1750 p.s.i.a. without catalysts and obtained aldehydes and acids primarily.
Paris (24) found that low oxygen to hydrocarbon ratios under high
pressures yielded methanol mainly.

2. Ethane

Ethane is found to oxidize more easily than methane. Alcohols, aldehydes, and acids corresponding to the ethane molecule are found in quantities larger than the products corresponding to the methane molecule in spite of a tendency towards a carbon to carbon bond rupture. Newitt and Townend (22) using approximately 8 to 1 ethane-oxygen at 520°F and 100 atm. obtained methanol and ethanol primarily with smaller amounts of both corresponding acids and aldehydes. Increased pressure favoured ethanol but reduced yields of methanol and formaldehyde.

3. Propane

Propane at 150 atm. reacts with oxygen at temperatures as low as 234°F according to Wiezevich and Frolich (32). This temperature increased to 304°F when the pressure was reduced to 33 atm. Products reported were acetaldehyde, formaldehyde, acetone, methanol, ethanol, propanol, butanol, acetic acid and formic acid. Higher pressures also favoured oxidation of the middle carbon atom in propane.

4. Butane and higher

Oxidation temperatures of butane are also reduced according to Wiezevich and Frolich (32). A hydrocarbon mixture with 95 per cent butane oxidized readily at temperatures of 410-490°F and pressures of 33-160 atmospheres. They report the identification of one-, two-, three- and four-carbon atom alcohols, acetaldehyde, propionaldehyde, acetone, acetic acid and propyl acetate. Lower pressures seemed to favour the formation of low molecular weight alcohols and acids whereas the higher

pressures favoured formation of higher moleculr weight alcohols
and aldehydes.

Oxidation of 60 per cent n-pentane and 40 per cent
isopentane at approximately 135 atm.and temperatures ranging from
570° to 930°F by Wiezevich and Frolich(32) gave little methanol and
formaldehyde but mainly acetaldehyde, methyl ethyl ketone, ethyl and
propyl alcohol and secondary amyl alcohols.

Some work has been done on higher individual hydrocarbons
by Wiezevich and Frolich (32), Wheeler and Blair (31) and other
authors, but this information reflects to an even greater extent the
difficulty in making overall interpretations of experimental oxidation
data.   The extensive work of Wiezevich and Frolich (32) unfortunately
is obscured by the use of impure feed stocks. The excellent review
by Egloff and associates (12) also summarizes other information, part
of which is presented intact here:

> In thermal oxidation of alkanes, increase of
> temperature resulted in a shorter induction period.
> Temperatures greater than those required for pyrolysis
> result in rupture of molecules....Slow heating presumably
> permits the early formation of products which initiate
> the reaction. Preheating the reactants before combining
> them does not shorten the induction period.
>
> The composition of the reacting mixture influences
> both the rate of oxidation and the amount of oxidation
> products formed.... If oxygen is in slight excess,
> variation in its concentration has little effect upon
> the oxidation but the presence of a great excess has

an inhibitory effect. Although the induction
periods of ethane and propane were longer when the
oxygen concentration was high, the reaction rate was
greater after the reaction began. Since rapid reaction
causes a temperature rise which is destructive to
liquid products already formed, high hydrocarbon
concentrations favour increased yields of partially
oxidized products.

Increased pressure influences hydrocarbon
oxidation by increasing the reaction rate, de-
activating chain carriers, altering electrostatic
field and directing a reaction so that less space
is required.

The literature includes extensive mention of oxidation
studies with solid and gaseous catalysts. A recent paper by Dodge
and co-workers (4) in which n-butane was catalytically oxidized
indicated olefinic oxygenated products which are not encountered in
the homogeneous non-catalytic oxidation studies discussed. Because
this phase of the butane partial oxidation project does not involve
catalytic reactions, no further mention of catalytic investigations
will be presented here.

It is worthwhile to mention that another recent summary
paper by Rust and Vaughn (26) describes an alternative method of
oxidation involving bromination. This paper is of interest because
it supports a peroxide mechanism and all of the postulated intermediates
were actually isolated.

PROCESS AND EQUIPMENT

General Details

This study of direct oxidation of hydrocarbons was started by Doctors D. Quon and D. B. Robinson of the Research Council of Alberta and University of Alberta staffs, respectively, using the facilities of the Department of Chemical and Petroleum Engineering, University of Alberta. The process details were selected and the main designs drawn up by them. Reference to Figure 1 will illustrate the essentials of the process flowsheet which will now be described very briefly.
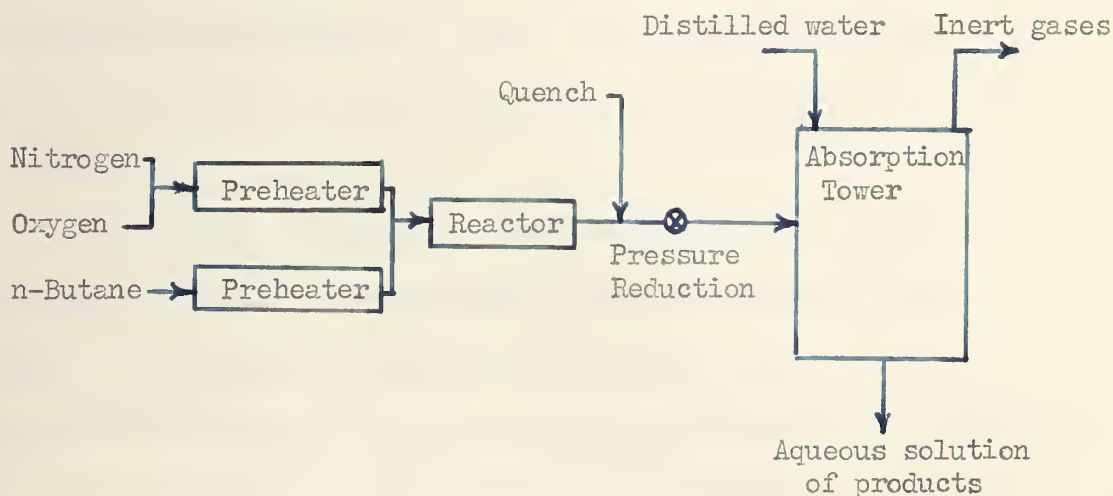
Figure 1.

The butane was to be oxidized in a homogeneous gas phase reaction with oxygen. High concentrations of inert nitrogen and

increased pressures were to be used in controlling the reaction
at non-inflammable concentrations. After preheating the butane and
nitrogen-oxygen mixture separately, the two streams were to be mixed
and introduced into the reactor at the reaction-initiating temperature.
The two streams entering the reactor from opposing directions impinged
upon each other and it was felt that sufficient turbulence was
generated to complete the mixing within a short length of the reactor.
The reactor, a vertical helical coil immersed in a boiling bath, was
designed to suppress the temperature rise of the exothermic reaction
with the cooling effect of the boiling bath. Upon leaving the reactor,
the products and unreacted gases were to be quenched with water and
cooled to terminate any further reactions. The pressure of the flow
system would then be reduced to atmospheric pressure and the low-
pressure stream would enter a packed absorption tower for removal of
useful products by absorption in water. The aqueous product solutions
could be withdrawn at the column base and the inert gases vented
from its head.

In 1950, R. G. Duthie, a graduate student in chemical
engineering, undertook the construction and installation of the
equipment. He carried out some preliminary runs but his results
were questionable because neither analytical techniques nor reaction
control were satisfactory. This experience did indicate some of the
equipment features which required modification.

Raw Materials

Nitrogen and Oxygen

These two gases were combined into a mixture of pre-
determined composition for simplicity in handling. Commercial
mixtures were found to be unsatisfactory because of delivery delays
and poor concentration reproducibility. To avoid this, nitrogen
containing 1-2 per cent and 6-10 per cent oxygen was purchased
separately, mixed to the desired oxygen content, and recompressed
in this laboratory. Under these conditions, oxygen concentrations
could be reproduced almost exactly.

The two cylinder discharges were individually metered with
two large calibrated rotameters, mixed in a short section of packed
pipe and then fed into the intake of a 3-stage 15 h.p. Rix Compressor.
Between mixer and compressor, an oil-sealed gasholder provided feed
storage for continuous compression. A small oil trap with blowdown
valve was installed after the compressor. From here, the compressed
gas was led directly to the nitrogen-oxygen storage cylinder manifold
which will be mentioned in the partial oxidation equipment layout.
Figures 2 and 3 show the mixing panel, gasholder, and compressor.

Some compressor oil did reach the cylinders with the re-
compressed mixture but after cooling and standing for a few days, no
oil droplets could be detected in the cylinder discharge. The vapour
pressure of the oil was insignificant.
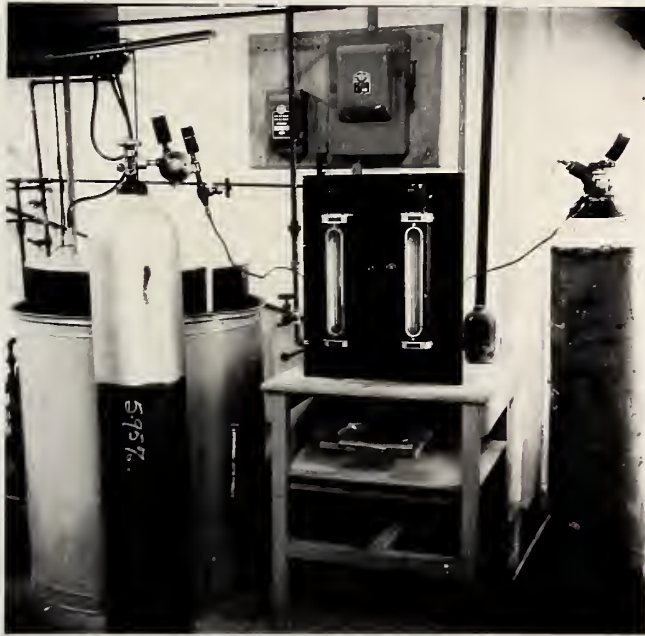
Figure 2.
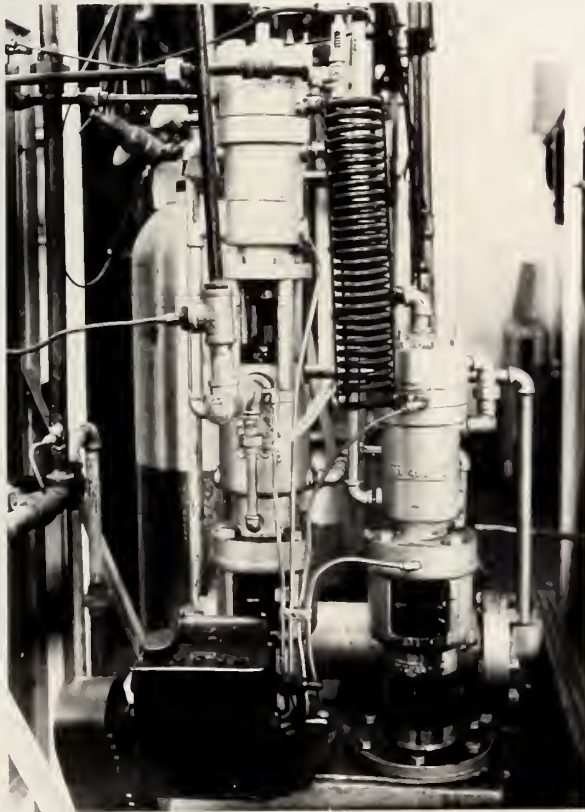
Figure 3.

n-Butane

All butane hydrocarbon used in this work was purchased from the Phillips Petroleum Company and was guaranteed 99 per cent n-butane. Impurities are stated to be iso-butane and iso-pentane but probably no higher than 0.3 per cent of each.

Water

Distilled water was used in all process streams other than ~~for~~ water-cooled condensers.

Details of Equipment

This section describes the features of the process equipment which was finally used in this study. Because all of the major equipment was modified and rebuilt and the process controls were improved, a detailed description of each part will be included. Figure 4 gives a diagrammatic picture of the equipment layout. Figures 5 and 6 show the process equipment and a combined view of the instrument panel and process equipment.

Butane and Water Storage and Measurement

Butane and water were stored under a nitrogen-pressurized atmosphere in vertical cylinders. The pressure of nitrogen within a commercial cylinder was reduced with an ordinary cylinder-attached pressure reduction valve to the storage pressure of 210 psig. Between this cylinder and the storage vessels, a ballast tank was inserted to maintain a uniform storage pressure. Under this pressure and room temperature, the butane remained in a liquid phase.
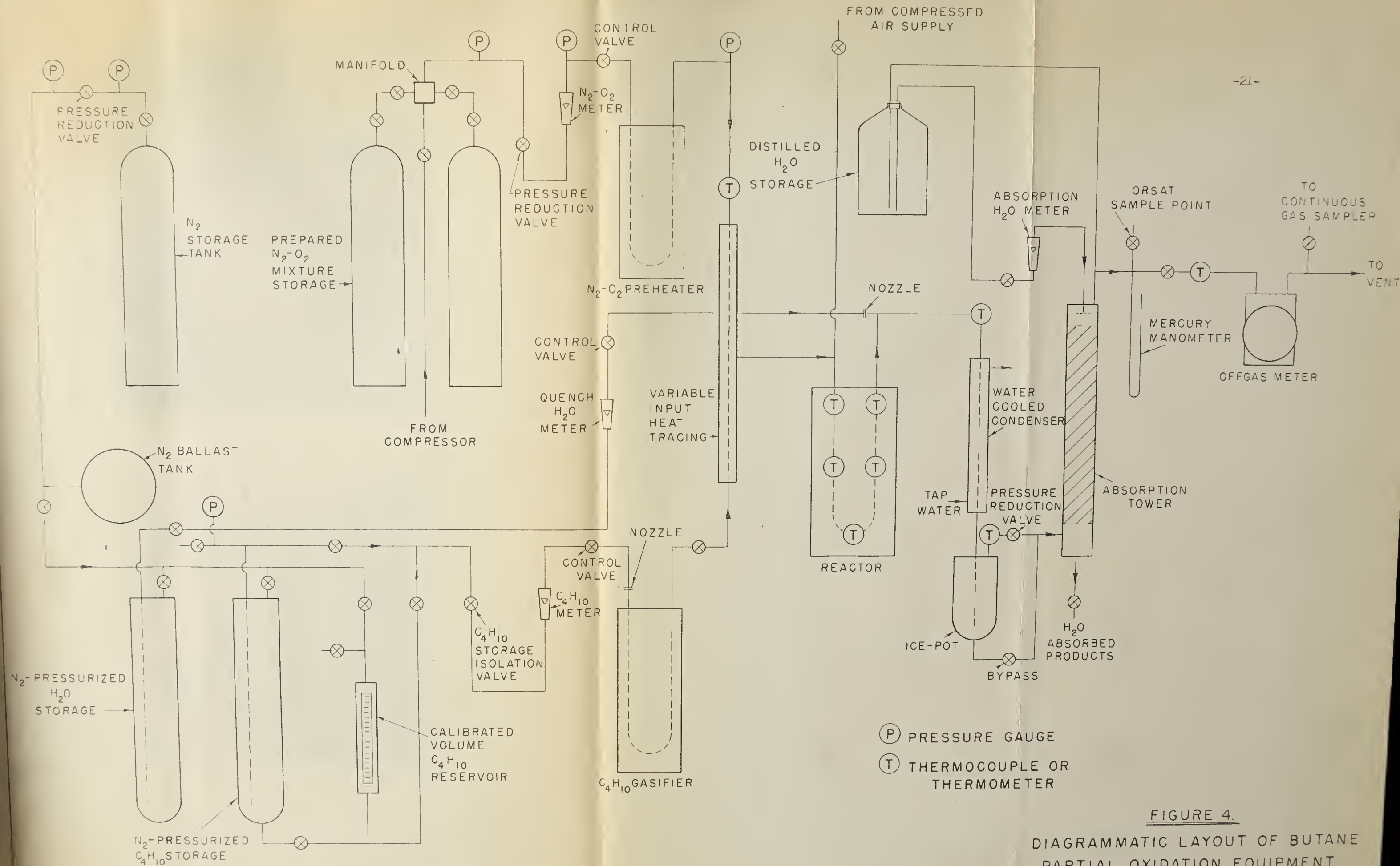
FIGURE 4.

DIAGRAMMATIC LAYOUT OF BUTANE
PARTIAL OXIDATION EQUIPMENT
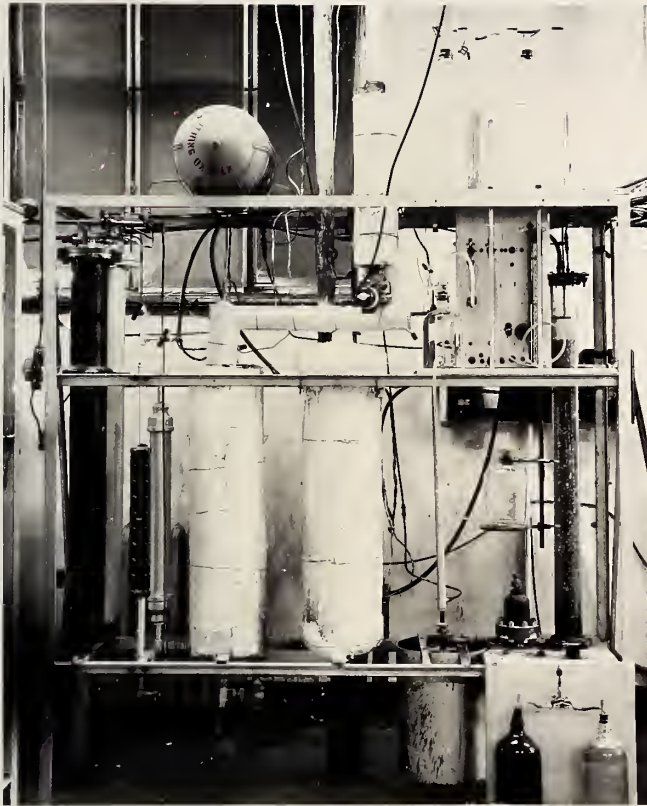
Figure 5.
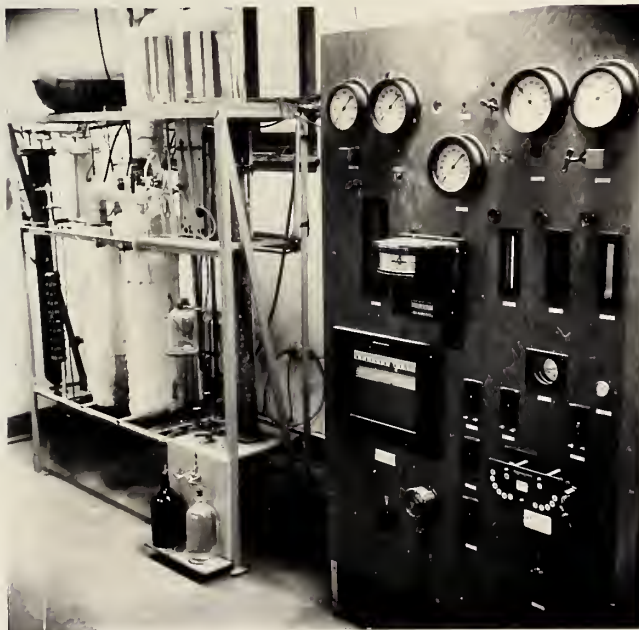
Figure 6.

Solubility data for nitrogen in liquid hydrocarbons (15) indicated
that the quantity of nitrogen which dissolved in the butane was
negligible.

Both storage vessels were constructed from a 48 inch length
of 4-inch schedule 40 iron pipe, flanged at the top and capped at the
base. The water cylinder was galvanized to prevent corrosion.
Both cylinders were connected to the same ballast nitrogen source
and their contents were discharged up through a section of standard
$\frac{1}{4}$-inch pipe, which extended internally from the top to nearly the base
of the storage vessels. The discharges were metered separately in
rotameters with the following maximum capacities:

<div align="center">

Butane   -   33 cc/min

Quench water -   37 cc/min

</div>

Needle valves for flow regulation were installed downstream from the
meters.

The water cylinder could only be charged by isolating it
and reducing its internal pressure to atmospheric. Distilled water
could then be poured into the vessel through a discharge line opening,
normally sealed with a threaded plug. To refill the butane cylinder
required isolating the cylinder and then bleeding off the excess
nitrogen gas while liquid butane was forced in from a nitrogen-
pressurized commercial cylinder. The commercial cylinder could be
connected to an extension on the discharge line of the butane storage
vessel.

Direct flow from this large butane storage vessel to the
process was required only during periods of preliminary operation.

For exact butane volume measurement, an auxiliary low capacity reservoir was made from standard 2-inch iron pipe. A Jerguson depth gauge was attached to this smaller vessel and a Lucite scale, graduated in 1/40 inch divisions, fitted over the gauge sight-glass so that the change in level could be accurately measured. After calibration, volume measurements accurate to 2 cc were easily obtained. This calibrated butane storage vessel was used during the measured operating periods and was refilled prior to each run. The butane was also pressurized with nitrogen from the previously mentioned source.

Provision was made for introducing water as a possible reactant diluent by drawing the fluid from the water storage vessel and metering it through another rotameter. However, because of time limitations, the present investigations did not include any runs on the effect of steam upon the reaction.

Nitrogen-Oxygen Storage and Measurement

Nitrogen-oxygen mixtures of desired composition were stored at pressures up to 2000 p.s.i.g. in commercial gas cylinders connected to a common manifold. The mixture storage pressure was reduced with a Cash spring-adjusted reducing valve, controlled by its downstream pressure. At the downstream pressure of 350 p.s.i.g., this feed was measured with a rotameter of 5.5 scfm capacity (at 60°F and 1 atm.) and regulated with a needle valve. The lines from the storage cylinders up to the reducing valve were 1/4 inch o.d. high pressure steel tubing.

Nitrogen-Oxygen Preheater

The nitrogen-oxygen feed preheater consisted of a U-shaped seven foot section of standard 1/4-inch type 304 stainless steel pipe, five inches between arms. The pipe surface was covered on the outside with a refractory material, a mixture of alundum powder and a concentrated aqueous solution of sodium silicate. This paste was spread over that surface which would be in contact with an electric heater. After drying and prolonged heating, the refractory fused to a very hard well-bonded layer. Ribbon type resistance windings were originally applied but overheating caused several earlier failures. A single wire-type chromel element, spring-wound, was wrapped helically about the insulating refractory and clamped to a terminal post at each end of the pipe. This form of heater proved satisfactory.

The entire unit was placed in a mild steel casing filled with an expanded mica insulation. The resistance of the heater measured 28 ohms and the energy input was controlled with a Burrell 2000 watt furnace transformer capable of delivering from 25 to 195 volts. An ammeter, mounted on the main panel, was connected to this circuit and two fuses protected the transformer.

Butane Gasifier

The butane gasifier was installed to vapourize and preheat the butane stream, facilitating reaction feed temperature control. The gasifier shell was made from a 22 inch length of standard three-inch iron pipe. Threaded pipe couplings, two inch and one inch nominal, were welded to the top and bottom, respectively, of the shell.

A 1000 watt 115 volt 3-position General Electric "Calrod" heating element was threaded into the bottom coupling. Copper tubing, 1/4 inch o.d. and 15 ft. long, was formed into a 2-1/2 inch diameter helical coil and placed inside the shell. The ends were drawn out through two small drilled openings and these holes were sealed by brazing the tubing to the shell wall. The heater was positioned in the center of this coil.

Three feet of standard two-inch iron pipe were fastened to the shell at the upper coupling. The interior of this extension contained 5-1/2 ft. of 1/4-inch copper tubing through which cooling water flowed. A vent from the head of this condenser was made with standard 1/2-inch iron pipe.

The shell was filled with liquid Aroclor (a chlorinated biphenyl boiling in the range 675-740°F and produced by Monsanto Chemicals) which was heated to boiling by the "Calrod" heater. The butane entered the helical coil through a 0.008 inch nozzle and was vapourized by the boiling bath. The bath vapours were condensed by the cold coil in the upper extension and volatile decomposition products were vented to the outside. This bath vapourized all of the liquid butane, and superheated the vapour up to 350-500°F depending upon the flow rate.

Variable Input Heat Tracing

The streams of nitrogen-oxygen and butane were now independently preheated but to different temperatures. The piping from the preheaters to their junction at the reactor inlet was heat traced to eliminate heat

losses and also to provide more exact control of the desired mixed
gas temperature.

This piping, standard 1/4-inch type 304 stainless steel,
was insulated with a thin layer of woven asbestos. Refractory
insulation was not used here because periodic dismantling of this line
was required. A single spring-wound chromel wire of 17 ohm resistance
was wrapped helically about the butane and nitrogen-oxygen piping.
Above this, a one inch layer of 85 per cent magnesia insulation was
applied. The energy input was controlled with a Variac transformer
rated at 5 amperes, 0-110 volts. An ammeter and two fuses were connected
to this circuit.

Reactor

The reactor consisted of a four inch diameter helical coil
containing 24 ft. of standard 1/4-inch type 304 stainless steel pipe.
This coil was inserted into a vertical shell made from standard six-
inch mild steel pipe with flanged necks welded at each end. A blind
flange with a single opening leading to a drain valve was attached to
the shell bottom. The shell top contained openings for the reactor
inlet and outlet, four thermocouple wells, and the bath condenser. All
openings but that of the condenser were sealed with threaded glands
containing graphite-wire packing. The cutaway view in Figure 7 shows
the reactor assembly and its internal details. The condenser shell
was made from standard two-inch iron pipe and its internal water cooler
from 1/4-inch copper tubing. A vent line was connected to the condenser
head.

WATER-COOLED
CONDENSER

FEED INLET

FEED OUTLET

PACKING GLANDS

THERMOCOUPLE
WELLS
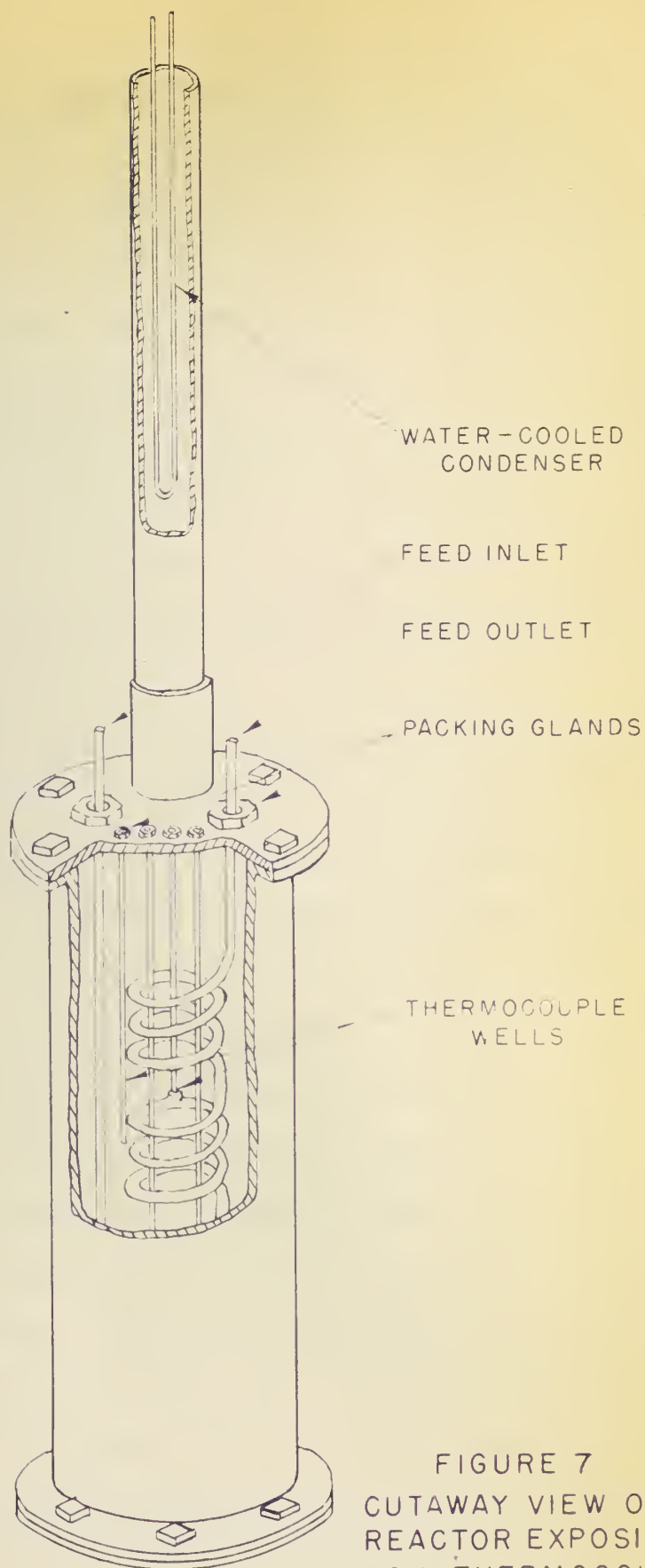
FIGURE 7
CUTAWAY VIEW OF
REACTOR EXPOSING
COIL,THERMOCOUPLE
WELLS AND BATH
CONDENSER.

The thermocouple wells were constructed from 1/4 inch o.d. stainless steel tubing, sealed at one end with silver-soldered stainless steel plugs. The sealed tips were silver-soldered into axial openings in machined plugs, externally threaded, so that 1/2 inch of the well protruded from the plug base. These plugs threaded tightly into couplings welded at three equal intervals in the length of the reactor pipe. The resultant thermocouple wells extended normal to the flow in the reactor. The open ends of the wells protruded from the shell top, the openings through the shell top being sealed with the packing glands. A fourth well extended directly from the shell top into the liquid bath filling the shell.

The inlet and outlet thermocouples were inserted in co-axial wells in the reactor piping, six inches from the feed junction and six inches from the outlet point. These wells were silver-soldered inside holes drilled into threaded stainless steel pipe plugs. Pipe crosses were connected to the ends of the reactor pipe to provide access for the two axial thermocouple wells.

The outer surface of the shell was insulated with the refractory material described earlier (see N_2-O_2 preheater) and two chromel ribbon-type resistance windings were helically wrapped side-by-side on the insulated shell surface. A further layer of refractory was placed over the windings. The entire reactor shell assembly was insulated with 1-1/2 inch 85 per cent magnesia block insulation.

The two windings measured 10.5 and 7.5 ohms resistance. The first winding was connected directly to a 110 volt energy source and

was used as an overload to shorten the time required to bring the
bath up to its boiling temperature. The energy input of the second
winding was controlled with a Variac transformer rated at 10 amperes,.
0-115 volts. Both circuits included two protective fuses.

The shell was two-thirds filled with Aroclor which immersed
all of the loops in the reactor coil. When boiling at constant temperature,
this bath suppressed the reaction temperature rise by absorbing the
exothermic heat of reaction. Details regarding use of Aroclor as a
heat transfer medium are included in the Appendix. Compressed air
and vacuum sources were also connected to the head of the bath condenser
so that the pressure of the boiling system could be altered if necessary
to maintain a constant boiling point.

By removing the condenser from the threaded coupling at its
base, the shell could be filled with Aroclor. The bath liquid could be
removed while hot by draining through the valve at the base of the shell.

Reaction Quench and Product Absorption

At the reactor outlet, a stream of liquid water was introduced
through a 0.008 inch nozzle. This mixture was cooled further by passing
down through an annular water jacket, three feet long, attached to a
section of the standard 1/4-inch stainless steel pipe. The cooled mixture
then flowed into a small receiver made from a 12 inch section of standard
three-inch pipe, capped at the base and flanged on top. This vessel was
termed "icepot" because it could be submerged in an ice bath; however
this additional cooling was found to be unnecessary.

Following the icepot, a spring-adjusted pressure reduction valve
reduced the system pressure to atmospheric pressure. A bypass was

connected from the ice-pot base to the downstream reduced pressure
line so that the ice-pot contents could be quickly withdrawn.

The cooled reaction products and inert gases at reduced
pressure entered the base of a packed absorption tower where the
~~soluble~~ oxygenated products were removed by solution in water.
Distilled water fed into the tower head and the aqueous products were
withdrawn into collection bottles from the base of the tower. The
inert gases passed into the vent line leaving the top of the absorption
tower.

The column was made from Pyrex brand glass pipe, three inch
i.d. four ft. long, packed with 1/4-inch ceramic Raschig rings.
Inlet and outlet fittings were threaded into plates which were held
in place with conical flanges at each end of the glass pipe. A pressure
equalizing line was connected from the column head to the distilled
water storage bottle. The difference in elevation between bottle and
column provided the necessary head to force the liquid through a rota-
meter, a needle valve and the distributor in the head of the column.

Offgas Measurement

The volume of offgas which was vented required exact measure-
ment. This was obtained by measuring the total volume with an accurately
calibrated displacement meter connected to the vent line. The temperature
of the gases at meter conditions was obtained with a Weston dial type
thermometer. The corresponding pressure was taken on a mercury manometer
connected to the absorption tower head.

Spot and composite gas samples for Orsat analysis were taken
prior to the meter but a larger sample, passed continuously through

an absorption train, was withdrawn from a point downstream from
the meter.

Temperature Measurement

All thermocouples were made with chromel-alumel junctions.
The important temperatures were recorded continuously on a Minneapolis-
Honeywell 8-point Electronic Temperature Recorder operating on a
four-minute cycle. The following temperatures were recorded: nitrogen-
oxygen preheat, reactor inlet (twice), 6 ft. in reactor, 12 ft. in
reactor, 18 ft. in reactor, reactor outlet and reactor bath. A Brown
indicating pyrometer was fitted with a thermocouple selector switch
so that a temperature could be obtained at any time of butane preheat,
quenched offgases and nitrogen-oxygen preheat.

Materials

All piping from the storage system to the preheaters consisted
of 1/4 inch o.d. copper tubing. From the preheaters through the
reaction system and up to the absorption tower, type 304 stainless
steel piping was used exclusively. All threaded joints were sealed
with ordinary pipe-sealing compound distributed by the Crane Company.
Graphite-base sealing compounds tested were found to be unstable at
high temperatures with consequent development of leaks. "Cranite"
gasket material was satisfactory for the term of service required here.

Process Control

Butane Feed

The regulation of the butane feed rate with a small rotameter and needle valve was not entirely satisfactory. Although steady flow rates could be maintained over the operating periods, the rotameter was not precise at the low rates. The rotameter calibration curve supplied with the instrument was inaccurate; consequently after each run, new points were plotted based on the average volume flow per unit time at the particular float reading. In spite of this precaution, the rotameter remained inexact at the lower rates because of poor float characteristics. Finally, a test measurement of the flow rate was adopted whereby the change in depth of the calibrated butane reservoir was observed over a timed interval preliminary to the actual experimental run.

The measured volumes were always corrected for changes in butane liquid density with temperature after measuring the reservoir surface temperature with a "Pyrocon" surface thermocouple.

Nitrogen-Oxygen Feed

The rotameter and needle valve which were used to regulate the nitrogen-oxygen feed rate were quite satisfactory. Errors in the flow rate were caused by the pressure reduction valve which reduced the storage cylinder pressure to the constant pressure required for flow measurement. This valve was designed to maintain a constant downstream pressure but in practice, the downstream pressure was found to increase

when the storage cylinder pressure decreased. During the test run, this resulted in an increasing flow rate. To eliminate this, the offgas meter flow was measured early in the run and the rotameter was adjusted at intervals to maintain this initial rate.

Feed Temperature

The two preheaters alone would not give a steady reactor feed temperature due to the heat losses from the piping between the preheaters and the reactor inlet.

Insulation of the line was not satisfactory because the large heat capacities of the two preheaters resulted in a considerable lag before any preheat adjustment could be felt. A small electrical winding was wrapped around this line, insulated and controlled with a Brown temperature indicator-controller but this setup caused a cycling in the preheat temperature which in turn caused a cycling in the reaction temperatures. Manual control of the variable input heat tracing, described earlier, alone was found to be satisfactory.

Continuous temperature readings at the reactor inlet thermo-couple were taken with a Leeds-Northrup potentiometer and any trends leading to a change in this temperature were anticipated and corrected by adjusting the heat tracing transformer. This procedure worked satisfactorily but required continuous vigilance from the operator.

Reaction Temperature

The highest temperature recorded on any of the reactor thermo-couples indicated the approximate position and extent of the temperature peak. The temperature distribution in the reaction zone was a function

of reaction conditions, gas composition and reactor design, and
hence could not be controlled independently.

Reaction Pressure

The reaction pressure was uniform during the majority of runs.
At the latter stages of operation, the pressure reduction valve after
the product quench and cooling caused variations in the reaction pressure
up to five psia. To offset these changes, further vigilance and
necessary adjustment of the valve spring was required.

Bath Temperature

With no exceptions, the bath temperatures were steady over
all operating periods. The bath temperatures of successive tests
would increase slightly because of Aroclor decomposition; however
the Aroclor boiling point was corrected by varying the bath pressure.
Nearly all of the runs were taken within a bath temperature range of
10 Fahrenheit degrees.

Analytical Equipment and Procedures

Orsat Gas Analyzer

After passage through the water absorption tower, the offgas
contained carbon dioxide, carbon monoxide, oxygen, unreacted hydro-
carbons, nitrogen and traces of other gases, such as unabsorbed products.
A standard Orsat containing liquid absorbents for carbon dioxide, un-
saturated hydrocarbons and oxygen and pipettes for both catalytic and
slow combustion of carbon monoxide, hydrogen and saturated hydrocarbons
did not give satisfactory analyses. The total volume of measurable

gases varied from 2 to 6 per cent and at these low concentrations, complete combustion was not easy to obtain and hence difficult to reproduce. The presence of higher saturated hydrocarbons interfered with absorption of unsaturated hydrocarbons in fuming sulfuric acid. Some hydrocarbon cracking or oxidation was found to occur when determining carbon monoxide by oxidation with a copper oxide catalyst at 290-300°C. For these reasons and also because of the time required for a complete analysis, the gas analyzer was modified so that rapid yet exact determinations could be made.

A Burrell cabinet-model gas analyzer was fitted with four absorption pipettes and a tapering volumetric burette. By measuring volumes in this burette over mercury and with an attached mercury compensating manometer, gas analyses could be measured to 0.02 per cent in the range 0-6 per cent. In the range, 6 to 22 per cent, the accuracy was 0.05 per cent. These figures were reproducible on the modified Orsat.

Carbon dioxide, unsaturated hydrocarbons, oxygen and carbon monoxide were measured in the offgas in the indicated sequence. Liquid absorbents were used in obtaining rapid analyses and with the exception of potassium hydroxide (for carbon dioxide) were purchased in ready-to-use form from the Burrell Company. The above sequence with the potassium hydroxide, Lusorbent, Oxsorbent and Cosorbent, absorbents, gave rapid and specific results (18).

Composite gas Sample

A continuous sample of scrubbed offgas was withdrawn from the absorption tower gas outlet and stored over a non-absorbing liquid in a bottle. Analysis of this sample served as a check on routine offgas

analyses for the particular operating conditions. Because both
process flows and sampling rate were constant, this analysis gave a
true average offgas composition.

A nearly saturated solution of sodium chloride in water,
containing one per cent hydrochloric acid and coloured with methyl
orange indicator, was used as the confining liquid. No absorption of
oxygen, carbon monoxide or hydrocarbons could be detected. However the
carbon dioxide concentration always decreased slightly and unless very
careful precautions were observed, the oxygen content of the sample
tended to be high.

Continuous Gas Absorption Train

To complete the offgas analysis, the determination of unreacted
hydrocarbons was required. Immediately after the offgas meter, a
continuous sample of offgas was drawn through an absorption system in
which the hydrocarbons were oxidized over a copper oxide catalyst to
carbon dioxide and recovered in a potassium hydroxide gas bubbler.
Figure 8 shows the absorption train and oxidation furnace.

The sample was first passed consecutively through 100 ml. of both
distilled water and 2, 4-dinitrophenylhydrazine solution in fritted glass
bubblers for determination of unabsorbed aldehydes (see Appendix). A
third bubbler containing 100 ml. of 3N KOH removed CO_2 after which an
entrainment trap was placed. The volume of the sample was now measured
with an accurately calibrated water-filled wet test meter. The distilled
water and acidic phenylhydrazine apparently absorbed insignificant
quantities of CO_2 because the KOH bubbler value for CO_2 checked with
the value obtained from the Orsat analysis of offgas.
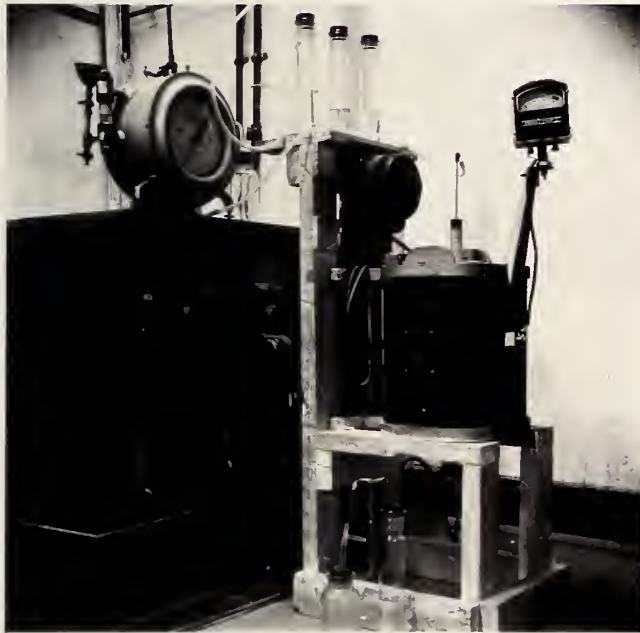
Figure 8.

The specially prepared copper oxide catalyst (see Appendix or reference 21) was packed in pellet form within a Vitreolite tube, one inch i.d. and two ft. long. The tube was vertically held within a Burrell high temperature furnace rated at 1.25 kva. The temperature of the furnace was controlled with a 10 amperes 0-115 volt Variac transformer and could be measured with an iron-constantan thermocouple placed in a Vitreolite thermocouple well, 1/4 inch o.d. This well was inserted upwards into the center of the furnace tube; however, it was not used once the corresponding furnace temperature-indicator reading was determined. Oxidation of hydrocarbons was performed at 700°C and catalyst re-oxidation with air at 400°C.

After the oxidation of the hydrocarbons and carbon monoxide was completed, the CO_2 produced was absorbed in 100 ml. of 3N KOH in another fritted glass bubbler placed after the furnace. A trap was placed downstream from this bubbler and a vacuum source was connected to the end of the train. Vacuum was required to maintain passage of the sample through the train because of the pressure drop across the four fritted glass bubblers. The vacuum source could be adjusted to any desired pressure differential and the flow regulated with a small Hoke rotameter of one liter pm capacity.

When sampling was discontinued, nitrogen was used to flush all of the measured sample through the furnace and final bubbler. Blank runs made with nitrogen showed that no errors resulted from its use. Tests made with two KOH bubblers in series indicated complete CO_2 absorption in the first bubbler.

Any hydrazone precipitated in the combined 2, 4-dinitro-phenylhydrazine and water bubblers was determined gravimetrically. The precipitate was filtered out, washed with a small volume of water and then air-dried prior to weighing. This weight of phenylhydrazone was taken to correspond directly to weight of acetaldehyde on a mole basis, i.e.

$$CH_3CHO + H_2N.HN.C_6H_5 \longrightarrow CH_3CHN.HN.C_6H_5\downarrow + H_2O$$

The KOH solution and distilled water used in washing the bubbler were transferred to a graduated cylinder for measurement of the total volume. Aliquot portions of this volume, usually 25 ml, were titrated with standardized HCl using a mixed and methyl orange indicators (see Appendix). This procedure involved neutralization of the excess KOH with approximately 3N HCl, to nearly the mixed indicator endpoint, and then titration to the mixed indicator yellow colour with standardized N/10 HCl. This endpoint gave the pH corresponding to formation of $NaHCO_3$. Then, by adding methyl orange indicator and completing the titration with the N/10 HCl to the first trace of orange colour, the CO_2 could be determined on a direct mole basis, i.e.

$$NaHCO_3 + HCl \longrightarrow NaCl + CO_2\uparrow + H_2O$$
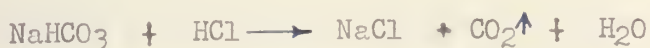
Ultimate Carbon Analysis

A special technique (27) whereby carbon content of volatile organic liquids could be obtained in a standard ultimate carbon apparatus was originally applied (see Appendix). In spite of exact duplication in repeat analyses with this method, the results were later found to disagree with the carbon contents calculated from mass spectrometer

analyses of the same solutions. Ultimate carbon content was accepted
on the mass spectrometer basis.

Operation of Equipment

A brief outline of the procedure followed in obtaining the
experimental data at one set of reaction conditions is presented in
this section. A detailed step-by-step procedure is appended to the
report.

For each run, the oxygen content of the nitrogen-oxygen
feed was determined with the Orsat. Knowing this value and the
desired butane-oxygen ratio, the feed rates could be calculated which
would give the desired feed space velocity at the particular reaction
pressure. The contraction or expansion in the volume of feed gas
caused by the reaction was never large so that the expected offgas
rate at offgas meter conditions could also be estimated.

Experimental data was taken during periods of constant or
nearly-constant offgas composition. This composition in some cases
was found to vary slightly because of the sensitive nature of the
reaction and/or defects in the control equipment which have already
been mentioned. The measured period of operation was usually commenced
when a uniform reactor temperature profile was being recorded. All
necessary data were recorded during this period and care was taken to
maintain steady state operation.

The continuous offgas absorption train which required a short
initial period of supervision was started a few minutes in advance.

During this period, the absorption tower and ice-pot were drained of any residual product solution. Upon commencing the timed interval, the calibrated butane reservoir and offgas meter readings were recorded. Following this, the absorption column product solution drain was switched to an empty collection bottle and the composite gas sample flow initiated. This equipment once started required little supervision.

The offgas was sampled and analyzed by Orsat three times during the period of operation, usually one hour.

The reactor inlet temperature was held equal to the reactor bath temperature by measuring it repeatedly with the potentiometer and adjusting, if necessary, the variable input heat tracing transformer.

The offgas meter discharge rate was timed at intervals with another stopwatch and the nitrogen-oxygen feed was returned to the initial rate when a change in offgas flow was noted.

The pressure reduction valve upstream from the absorption tower was re-adjusted if the reaction pressure varied.

All conditions of gas volume measurement were checked at intervals and recorded.

At the conclusion of the operating period, all sampling was stopped and the final volume of the offgas absorption train sample was noted. This train was then purged with nitrogen to force all of the measured sample through the combustion furnace. These steps and drainage of the ice-pot and absorption tower were performed prior to taking the final stopwatch reading. When this reading was taken, the final offgas meter and butane reservoir readings were recorded.

The product collection bottle was disconnected and sealed for storage.

The composite gas sample was analyzed with the Orsat as early as possible. The KOH solutions from the CO_2 bubblers were titrated and aldehydes in the offgas determined gravimetrically when convenient.

EXPERIMENTAL RESULTS

Scope of the Investigation

The experiments were designed to explore the effects of
pressure, reaction time and feed composition, at a fixed initiation
temperature, upon the partial oxidation of butane. The scope of the
work was restricted by the equipment limitations, viz. maximum pressure
of 200 psia., reaction times of 0.8 to 4.5 sec. and non-inflammable
feed compositions. Inflammability limits for butane-oxygen-nitrogen
mixtures (9) could not be accurately calculated but concentrations of
oxygen below six per cent would certainly be below the lower limit
for oxygen. Low oxygen concentrations would also facilitate the
temperature control of the single-pass reaction. Preliminary work by
Duthie (10) involved a two to one oxygen to butane feed ratio -
six per cent oxygen and three per cent butane - and this mixture was
found to be very reactive. Faith (14) indicates that at 23 atm.,
commercial oxidations of butane are performed with a 140 to 1 ratio of
inerts to butane and air to butane ratio of 0.10 to 1. To produce
nitrogen-oxygen mixtures in this laboratory, nitrogen could not be
purchased locally with less than 1.5 per cent oxygen impurity and
further purification was difficult. It was therefore decided to
work with both oxygen and butane concentrations in the range, 1.5 to
6 per cent. Nitrogen was always used as the inert gas.

To determine the effect of feed composition, a pressure of 100 p.s.i.a. and reaction time of 3.0 sec. were selected because preliminary work had indicated that these concentrations were in the region suitable for good liquid product yields. Either oxygen or butane, in turn, was held at three per cent and the other component was varied from 1.5 to 6 per cent. A further series of tests was made with a butane to oxygen ratio of one to one but varying the butane (and oxygen) concentration from 1.5 to 6 per cent to study the effect of total reactant concentration upon the reaction.

With butane to oxygen ratio of one to one and a reaction time of 3.0 sec., the pressure was varied from 50 to 175 p.s.i.a. For the same feed composition but pressure fixed at 100 p.s.i.a., the reaction time was varied from 0.8 to 4.5 sec.

Definitions

Frequent use of certain terms has been and will be made in this report. To avoid ambiguity in interpretation, the applicable definitions of these terms are included:

Space velocity is the ratio of volume of feed gases per unit time at NTP to the volume of the reactor and has the dimension of reciprocal hours.

Reaction time implies the period of time in seconds during which the reactants and products are exposed to the reaction conditions. This calculated value is approximate because it was based on the offgas flow rate but contraction or expansion of the feed gas was always very

slight. The reaction peak for 3.0 sec. always occurred early in the reactor so that the offgas volume is the better value on which to base reaction time. One indeterminate error arises from the expansion of the gases caused by the heat of reaction. This results in an increased gas velocity and shorter reaction time but does not introduce more than five per cent error in the calculated reaction time. In most cases, a contraction of the feed volume occurred during the reaction and this would tend to compensate for some of this error.

Reaction temperature refers to the temperature of the reactants and/or products while in the reactor and was found to vary during the course of the reaction. The reactor temperature profile maps this temperature relative to its position within the reactor.

Reaction initiating temperature is adjusted to be equal to the temperature of the bath in the reactor shell.

Reaction yields are calculated as gm-mol of a particular compound produced per 100 gm-mol of feed. The feed composition is subject to variation.

Carbon conversion is the percentage of the total number of gm-atoms of carbon in the feed which is converted to a particular compound or group of compounds.

Selectivity of the reaction may be regarded as the reaction efficiency. The "reaction" stated here implies production of oxygenated carbon compounds and the term refers to the percentage of the total gm-atoms of carbon in these compounds which is contained in a particular compound or group of compounds.

Unreacted saturated hydrocarbons are assumed to be normal
butane for establishing the overall carbon balance.

Unreacted unsaturated hydrocarbons are assumed to be ethylene
for establishing the overall carbon balance. Data on the pyrolysis of
normal butane at the bath temperature (16) indicate that ethylene
is more likely to be the main olefin produced rather than propylene
or butylene.

Heat of reaction for the particular operating conditions of
each run was calculated from an enthalpy balance on the gases
passing through the reactor.

Induction period of the reaction was interpreted as the time
elapsing between the junction of the butane and nitrogen-oxygen streams
at the reactor inlet and the first appearance within the reactor of a
temperature greater than that of the bath.

Useful products is a collective term referring to the oxygenated
organic compounds which were reported in the aqueous product solutions.

Applicability of the Data

The reaction data obtained for some of the runs are not
entirely satisfactory. In spite of the rather detailed precautions to
ensure the desired feed composition, feed rate, inlet temperature and
reaction pressure, variation in the offgas analysis was noted for some
of the runs. For the reaction times of 3.0 sec., slight changes in
this variable are of little consequence because of the near-completion
of the reaction in the first half of the reactor.

For each trial, certain measurements are believed to be accurate.
These independent measurements comprised: volume of butane introduced to
the reactor, per cent oxygen in the nitrogen-oxygen mixture, total

volume of offgas, length of the test run and offgas and product
solution analyses.

Reliable individual gas analyses were obtained with the
modified Orsat providing proper techniques were employed. Agreement
between the composite sample analysis and an integrated average of the
spot sample analyses usually was quite good with the exception of
oxygen content. Much of the error in oxygen balances may be traced to
slight composite sample contamination with air when transferring the
sample from the bottle to the Orsat burette. The introduction of a
few cc. of air would not affect the analyses of offgas constituents
other than oxygen. The Orsat CO_2 results also checked with the CO_2
content reported in the offgas absorption train.

The titration of the KOH bubblers for determination of unreacted
hydrocarbons and CO required an exact interpretation of the endpoint.
The offgas and wet test meters were calibrated exactly and care was
exercised in maintaining uniform sampling conditions to eliminate
error in the multiplying factor. Earlier in this work ultimate carbon
analysis of the liquid products was adopted in order to establish the
carbon balance. These balances were found to be 5 to 10 per cent low
and an erroneous mixed indicator endpoint was suspected. Accordingly,
the titrations were adjusted to the mixed indicator colour just prior
to the true endpoint and satifactory carbon balances were obtained.
This misconception resulted from the belief that the $NaHCO_3$ endpoint
occurred at a pH of 8.3 rather than 8.4 (mixed indicator: endpoint is
8.4). In the later stages of this work, when the mass spectrometer
analyses were received, the ultimate carbon analyses accepted earlier

were shown to be low. Because product and offgas analyses are
believed accurate, all carbon balances have been adjusted equal to the
carbon in the measured butane feed. The error has been taken up by the
unreacted hydrocarbon analyses which are known to be high.

The carbon content of the solutions was calculated from the
mass spectrometer analyses. The identification of compounds with
the mass spectrometer may be taken as reliable (29). Alcohols are
identified positively but aldehydes may be subject to some error.
For instance, the identification of acetaldehyde could result from a
combination of several possible constituents - carbon dioxide, ethylene
oxide or acetal. Carbon dioxide dissolved in the solutions should be
negligible relative to the quantities of acetaldehyde reported. Ethylene
oxide will introduce no error because its molecular weight and atomic
constituents are identical to those of acetaldehyde. In any case,
it is reported as a trace constituent in commercial propane and butane
oxidation. The presence of acetal is indeterminate at present but
its formation usually requires an acidic solution and heat. The
dilute aqueous solution should also minimize the chance of its formation;
hence it was assumed absent.

Practically all aldehydes and acids have a peak in common with
that identified as formic acid. Most of these compounds have higher
molecular weights than that predicted by the analyst so that formic
acid appeared the most likely suspect. Although formaldehyde is
commonly reported as a product of hydrocarbon oxidations, it could
not be easily mistaken for one of the other major components reported.
It could be present as a trace constituent but the solutions analyzed
were too dilute for positive detection.

Compounds reported as useful products were methanol, ethanol, acetaldehyde, acetone and formic acid. Methanol and acetaldehyde are reported in large quantities but the minor products' quantitative determination may not be too accurate because the water content of the samples was usually higher than 99 mol per cent. Concentrations of these compounds were reported in the range 0.05 to 0.10 mol per cent and their analyses were adjusted slightly for the total to equal 100 mol per cent.

Treatment of Data

Results of all calculations are presented in tabulated form for the five series of investigations: effects of pressure, reaction time, butane, oxygen and concentration. A representative treatment of the experimental data procured in a single run is appended to the report.

To facilitate the chemical interpretation of the reaction, graphs were plotted for each series. The process variable, pressure, etc., under examination was always plotted as the abscissa and the corresponding change in a particular property was plotted as the ordinate. The following experimental data were plotted directly: offgas composition, individual useful product yields and carbon dioxide and carbon monoxide yields. Best-fitting curves were shown on the above plots. To obtain the best-fitting yield curve for total useful products, the ordinates were obtained from the cumulative values of the individual useful product yields. Corrected yields were now available for CO_2, CO and total useful products at any value of the variable

under consideration. From these corrected yields, the carbon
conversion and selectivity of reaction were calculated and plotted.
It was considered better to obtain the data for these graphs from the
smooth curves rather than from the original data.

In using the recorded temperatures (see Figure 9) obtained
for the reactor temperature profile, an attempt was made to correct
the recorded temperatures for error caused by heat losses from the
well through conduction and radiation. The derivation of the correction
factor is shown in the appendix. Corrected temperature profiles
were plotted for each series of runs.

The tabulated experimental results are shown in Tables 1
to 5.

Table 1

Effect of Pressure

Run No.	A-1	4-A	12-A	9-A	10-A	11-A
Duration (min)	Start up	68.0	57.6	50.4	39.9	43.3
Gm-mol offgas (dry)	–	62.4	71.4	78.1	71.9	92.2
Gm-mol feed gas (dry)	–	63.0	71.7	79.2	73.0	93.6
Inlet temperature ($°F$)	726.5	726.5	726	724	726.5	724
Bath temperature ($°F$)	727	727	723.5	723	723	723.5
Reactor pressure (psia)	50	75	100	125	150	175
Nominal reaction time (sec)	3.0	2.9	3.0	3.0	2.9	3.1
Space Velocity (hr^{-1})	–	2540	3410	4310	5010	5820
Feed Rate (Gm-mol/hr)	–	55.6	74.7	94.5	110	130

Feed gas (mol % dry)

	A-1	4-A	12-A	9-A	10-A	11-A
N_2	94.00	94.02	94.34	93.92	94.00	94.03
O_2	3.00	2.98	3.02	3.00	3.00	3.00
C_4H_{10}	3.00	3.00	2.64	3.08	3.00	2.97

Offgas (mol % dry)

	A-1	4-A	12-A	9-A	10-A	11-A
CO_2	nil	0.52	0.64	0.62	0.63	0.58
CO	nil	0.45	0.70	0189	1.07	1.32
O_2	3.00	1.97	1.54	0.78	0.24	0.05
Unsaturates	nil	0.35	0.44	0.48	0.52	0.61

Adjusted Carbon balance (gm-atoms C) —based on duration of run

		A-1	4-A	12-A	9-A	10-A	11-A
C in			7.58	7.56	9.76	8.76	11.12
C out	as CO_2		0.32	0.45	0.49	0.45	0.54
	as CO		0.29	0.50	0.69	0.77	1.22
	as U.H.C.		4.36*	5.90	7.33	6.65	8.21
	as U. Products		2.61*	0171	1.25	0.89	1.15
Total out			7.58	7.56	9.76	8.76	11.12

	A-1	4-A	12-A	9-A	10-A	11-A
Ratio of Carbon out to Carbon in		1.23	1.05	0.96	0.96	0.97

On basis of 100 gm-mol feed
Yield (gm-mol/100 gm-mol)

	A-1	4-A	12-A	9-A	10-A	11-A
CO_2		0.51	0.64	0.61	0.62	0.57
CO		0.46	0.70	0.88	1.05	1.30
Methanol		0.877	0.175	0.404	0.404	0.338
Ethanol		0.303	0.066	0.086	0.073	0.079
Acetaldehyde		1.25	0.190	0.326	0.172	0.223
Acetone		–	0.066	0.086	0.073	0.079
Formic Acid		–	0.087	–	0.110	0.079
Total Useful Products		2.43	0.58	0.90	0.83	0.80

Table 1 (continued)

Oxygen balance (to determine H_2)-gm-mol O_2

O_2 in	2.98	3.02	3.00	3.00	3.00
O_2 out	3.90	2.85	2.36	1.85	1.71
Difference	+0.92	−0.17	−0.64	−1.15	−1.29
Difference as gm-mol water	−	0.34	1.28	2.30	2.58

Hydrogen balance (check)-gm-mol H_2

H_2 in	15.00	13.20	15.40	15.00	14.85
H out	13.71	11.63	14.65	15.09	14.91
Difference	−1.29	−1.57	−0.75	−0.09	−0.06

Per cent O_2 reacted	34.6	49.4	74.4	92.0	98.3

ΔH of reaction (Kcal/100 gm-mol)

−117.9 *	−99.5	−166.5	−220.5	−221.3

* Mass spectrograph analysis inexplicably high. This value affects the reported unreacted hydrocarbons, the balances and lastly, the heat of reaction.

Table 2

Effect of Reaction Time

Run No.	A-2	6-A	B-4	12-A	8-A
Duration (min.)	Start up only	44.8	69.1	57.6	54.6
Gm-mol offgas (dry)	–	141.0	172.8	71.4	43.1
Gm-mol feed gas (dry)	–	141.4	172.4	71.7	43.6
Inlet temperature (^{o}F)	723	723	729	726	726
Bath temperature (^{o}F)	723	723	726	723.5	724
Reactor Pressure (psia)	100	100	100	100	100
Nominal reaction time (sec.)	0.8 & 1.0	1.2	1.4	3.0	4.5
Space velocity (hr^{-1})	–	8610	6840	3401	2190
Feed rate (gm-mol/hr.)	–	189	150	74.7	47.9

Feed gas (mol % dry)

	A-2	6-A	B-4	12-A	8-A
N_2	94.00	93.98	93.89	94.34	93.62
O_2	3.00	3.10	2.91	3.02	3.02
C_4H_{10}	3.00	2.92	3.20	2.64	3.36

Offgas (mol % dry)

	A-2	6-A	B-4	12-A	8-A
CO_2	traces	0.12	0.32	0.64	0.66
CO	traces	0.20	0.57	0.70	0.83
O_2	≈ 3.00	2.69*	2.49*	1.54	1.18
Unsaturates	nil	0.14	0.27	0.44	0.38

Adjusted Carbon balance (gm-atom C) -based on duration of run

		6-A	B-4	12-A	8-A
C in		16.48	22.08	7.56	5.88
C out as CO_2		0.17	0.55	0.45	0.28
as CO		0.28	0.99	0.50	0.36
as U.H.C.		14.93	19.40	5.90	4.62
as Useful Products		1.10	1.14	0.71	0.62
Total out		16.48	22.08	7.56	5.88

		6-A	B-4	12-A	8-A
Ratio of Carbon out to Carbon in		0.77	0.92	1.05	1.00

On basis of 100 gm-mol feed

Yield (gm-mol/100 gm-mol)

			6-A	B-4	12-A	8-A
CO_2			0.12	0.32	0.64	0.65
CO			0.20	0.57	0.70	0.82
Methanol			0.136	0.303	0.175	0.253
Ethanol			0.062	0.053	0.066	0.127
Acetaldehyde			0.260	0.053**	0.190	0.203
Acetone			–	0.036	0.066	0.127
Formic Acid			–	0.036	0.087	0.127
Total Useful Products			0.46	0.48	0.58	0.84

Oxygen balance (to determine H_2O) -gm-mol O_2

O_2 in	3.10	2.91	3.02	3.02
O_2 out	3.23	3.35	2.85	2.71
Difference	+0.13	+0.44	-0.17	-0.31
Difference as gm-mol water	-	-	0.34	0.62

Hyrdrogen balance (check) -gm-mol H_2

H_2 in	14.60	16.00	13.20	16.80
H_2 out	14.12	14.95	11.63	15.30
Difference	0.48	1.15	1.57	1.50

Percent O_2 reacted	19.3[1]	14.4[1]	49.4	61.2

ΔH of reaction (kcal/100 gm-mol)	-23	-50.2	-99.5	-120.3

* The high O_2 concentration in offgas resulted in not too satisfactory steady state operation. Errors may be attributed to more than one component.

** This acetaldehyde yield is known to be low because the unabsorbed aldehyde sample was spoiled

[1] The large error in O_2 in offgas is reflected here.

Table 3

Effect of Concentration

Run No.	3-A	12-A	7-A	B-7
Duration (min.)	Start up only	57.6	41.8	73.7
Gm-mol offgas (dry)	–	71.4	53.0	84.2
Gm-mol feed gas (dry)	–	71.7	54.2	87.0
Inlet temperature (°F)	726.5	726	726.5	725
Bath temperature (°F)	727	723.5	727	725
Reactor pressure (psia.)	100	100	100	100
Nominal reaction time (sec.)	3.0	3.0	2.9	3.3
Space velocity (hr-1)	–	3410	3560	3230
Feed rate (gm-mol/hr.)	–	74.7	78.0	70.9

Feed gas (mol % dry)

	3-A	12-A	7-A	B-7
N_2	97.00	94.34	90.70	87.50
O_2	1.50	3.02	4.67	6.15
C_4H_{10}	1.50	2.64	4.63	6.35

Offgas (mol % dry)

	3-A	12-A	7-A	B-7
CO_2	nil	0.64	0.90	1.13
CO	nil	0.70	1.22	2.63
O_2	1.50	1.54	1.15	0.39
Unsaturates	nil	0.44	0.70	0.76

Adjusted Carbon balance (gm-atom C) –based on duration of run

		12-A	7-A	B-7
C in		7.56	10.04	22.12
C out as CO_2		0.45	0.48	0.95
as CO		0.50	0.76	2.21
as U.H.C.		5.90	6.80	16.82
as Useful Products		0.71	2.00	2.14
Total out		7.56	10.04	22.12

		12-A	7-A	B-7
Ratio of Carbon out to Carbon in		1.05	1.09	0.91

On basis of 100 gm-mol feed

Yield (gm-mol/100gm-mol)

		12-A	7-A	B-7
CO_2		0.64	0.88	1.09
CO		0.70	1.40	2.54
Methanol		0.175	1.26	0.593
Ethanol		0.066	0.195	0.216
Acetaldehyde		0.190	0.533[1]	0.939[11]
Acetone		0.066	0.124	0.057
Formic Acid		0.087	–	–
Total Useful Products		0.58	2.11	1.81

Oxygen balance (to determine H_2O) -gm-mol O_2

O_2 in	3.02	4.67	6.15
O_2 out	2.85	3.75	3.64
Difference	o.17	0.92	2.51
Difference as gm-mol water	0.34	1.84	5.02

Hydrogen balance (check) -gm-mol H_2

H_2 in	13.20	23.1	31.8
H_2 out	11.63	23.5	32.7
Difference	-1.57	+0.5	+0.9

Per cent O_2 reacted	49.4	76.0	93.7
ΔH of reaction (kcal/100 gm-mol)	-99.5	-185.9	-461.7

    [1] Acetaldehyde yield known to be low because unabsorbed aldehyde sample was spoiled.

    [11] Acetaldehyde appears too high. Unabsorbed aldehyde sample may be in error.

Table 4

Effect of Butane

Run No.	17-A	12-A	16-A	B-6
Duration (min.)	50.1	57.6	41.0	72.7
Gm-mol offgas (dry)	59.4	71.4	51.0	83.8
Gm-mol feed gas (dry)	59.8	71.7	51.9	85.2
Inlet temperature (°F)	726.5	726	722	729
Bath temperature (°F)	730	723.5	727	725
Reactor pressure (psia.)	100	100	100	100
Nominal reaction time (sec.)	3.1	3.00	3.0	3.4
Space velocity (hr.$^{-1}$)	3270	3410	3460	3210
Feed rate (gm-mol/hr.)	71.5	74.7	75.9	70.4

Feed gas (mol % dry)

	17-A	12-A	16-A	B-6
N_2	95.57	94.34	92.32	89.05
O_2	3.06	3.02	3.09	3.58
C_4H_{10}	1.37	2.64	4.59	7.37
Butane-oxygen ratio	0.45	0.88	1.49	2.06

Offgas (mol % dry)

	17-A	12-A	16-A	B-6
CO_2	0.43	0.64	0.61	0.68
CO	0.29	0.70	0.63	1.04
O_2	1.83	1.54	0.66	0.43
Unsaturates	0.19	0.44	0.64	0.97

Adjusted Carbon balance (gm-atom C) -based on duration of run

	17-A	12-A	16-A	B-6
C in	3.26	7.56	9.52	25.16
C out as CO_2	0.26	0.45	0.31	0.57
as CO	0.17	0.50	0.32	0.87
as U.H.C.	2.52	5.90	8.08	22.90
as Useful Products	0.31	0.71	0.81	0.82
Total out	3.26	7.56	9.52	25.16

Ratio of carbon out to carbon in

	17-A	12-A	16-A	B-6
	1.17	1.05	0.96	0.82

On basis of 100 gm-mol feed

Yield (gm-mol/100 gm-mol)

	17-A	12-A	16-A	B-6
CO_2	0.43	0.64	0.60	0.67
CO	0.29	0.70	0.62	1.02
Methanol	0.041[1]	0.175	0.332	0.350
Ethanol	0.041	0.066	0.118	0.087
Acetaldehyde	0.168+	0.190	0.260	0.087[11]
Acetone	0.041	0.066	0.118	0.065
Formic Acid	0.041	0.087	0.118	0.065
Total Useful Products	0.33	0.58	0.95	0.65

Oxygen balance (to determine H_2O) -gm-mol O_2

O_2 in	3.06	3.02	3.09	3.58
O_2 out	2.58	2.85	2.21	1.97
Difference	-0.48	-0.17	-0.88	-1.61
Difference as gm-mol water	0.96	0.34	1.76	3.22

Hydrogen balance (check) -gm-mol H_2

H_2 in	6.85	13.20	22.95	36.85
H_2 out	6.84	11.63	23.20	33.13
Difference	-0.01	-1.57	0.25	-3.72

Percent O_2 reacted	40.5	49.4	75.5	88.3

Δ H of reaction (kcal/100 gm-mol)-111.2 -99.5 -175.4 -228.3

[1] This mass spectrometer analysis indicates the lack of quantitative differentiation between individual yields when water content of sample was high.

[11] Acetaldehyde sample known to be low because offgas aldehyde sample was spoiled

† Acetaldehyde yield is inexplicably high.

Table 5

Effect of Oxygen

Run No.	2-A	12-A	15-A	1-A
Duration (min.)	74.6	57.6	52.4	70.9
Gm-mol offgas (dry)	101.3	71.4	66.5	86.50
Gm-mol feed gas (dry)	103.7	71.7	67.4	88.4
Inlet temperature ($^\circ$F)	714.5	726	730	714
Bath temperature ($^\circ$F)	713	723.5	733	711.5
Reactor pressure (p.s.i.a.)	100	100	100	100
Nominal reaction time (sec.)	2.9	3.0	2.8	3.1
Space velocity ($hr.^{-1}$)	3730	3410	3520	3420
Feed rate (gm-mol/hr.)	81.8	74.7	77.2	74.8

Feed gas (mol % dry)

	2-A	12-A	15-A	1-A
N_2	95.59	94.34	92.79	91.32
O_2	1.58	3.02	4.65	5.85
C_4H_{10}	2.83	2.64	2.56	2.85
Oxygen-butane ratio	0.56	1.14	1.82	2.04

Offgas (mol % dry)

	2-A	12-A	15-A	1-A
CO_2	0.15	0.64	0.72	0.83
CO	0.04	0.70	0.71	1.20
O_2	1.34	1.54	2.38	2.69
Unsaturates	nil	0.44	0.41	0.42

Adjusted carbon balance (gm-atom C) -based on duration of run

	2-A	12-A	15-A	1-A
C in	11.52	7.56	6.88	10.08
C out as CO_2	0.15	0.45	0.48	0.72
as CO	0.04	0.50	0.47	1.04
as U.H.C.	9.92	5.90	5.13	5.66
as Useful Products	1.41	0.71	0.80	2.66
Total out	11.52	7.56	6.88	10.08

Ratio of Carbon out to Carbon in

	2-A	12-A	15-A	1-A
	1.36	1.05	0.91	1.23

On basis of 100 gm-mol feed

Yield (gm-mol/100 gm-mol)

	2-A	12-A	15-A	1-A
CO_2	0.15	0.64	0.71	0.81
CO	0.02	0.70	0.70	1.17
Methanol	0.131	0.175	0.304	0.881
Ethanol	0.131	0.066	0.093	0.205
Acetaldehyde	0.500	0.190	0.164	0.821
Acetone	-	0.066	0.093	0.102
Formic Acid	-	0.087	0.093	-
Total Useful Products	0.76	0.58	0.75	2.01

Oxygen balance (to determine H_2O) -gm-mol O_2

O_2 in	1.58	3.02	4.65	5.83
O_2 out	1.88	2.85	2.65	5.10
Difference	0.30	-0.17	-2.00	-0.73
Difference as gm-mol water	-	0.34	4.00	1.46

Hydrogen balance (check) -gm-mol H_2

H_2 in	14.40	13.30	12.80	12.60
H_2 out	14.26	11.63	15.09	13.62
Difference	-0.14	-1.57	+2.29	+1.02

Per cent O_2 reacted   15.8   49.4   74.9   54.9

ΔH of reaction (kcal/100 gm-mol)

                -89.0   -99.5   -313.5   -245.9

   [1] These mass spectrometer analyses are part of a group which were all inexplicably high. They were disregarded when plotting graphs.

DISCUSSION

Chemical Effects

The interpretation of the data is restricted to the recognition of the chemical effects associated with butane oxidation under the test conditions. Linking of these observations to a suitable reaction mechanism is not proposed at the present time.

Effect of Pressure

Graphs 1 to 5 and Figure 9 show the reaction trends associated with pressure increase for a reaction time of 3.0 sec. and feed composition of three per cent of both oxygen and butane. The bath temperatures varied from 723 to 727°F.

At 50 psia no noticeable reaction occurred but as the pressure was increased, the mixture became increasingly more reactive until 175 psia was reached at which point the oxygen remaining after reaction was insignificant. As may be expected, the reaction rate increases noticeably because the temperature profile peaks must shift towards the reactor inlet to account for the lower temperatures for the 150 and 175 psia runs at the 6 ft. position and their increased heats of reaction. The 150 and 175 psia runs yielded equal heats of reaction, showing a limiting condition, and also gave identical temperature profiles which fact supports the heat of reaction calculations.

This limiting condition may be the oxygen available for reaction which limits the initial temperature rise and the total amount of reaction.
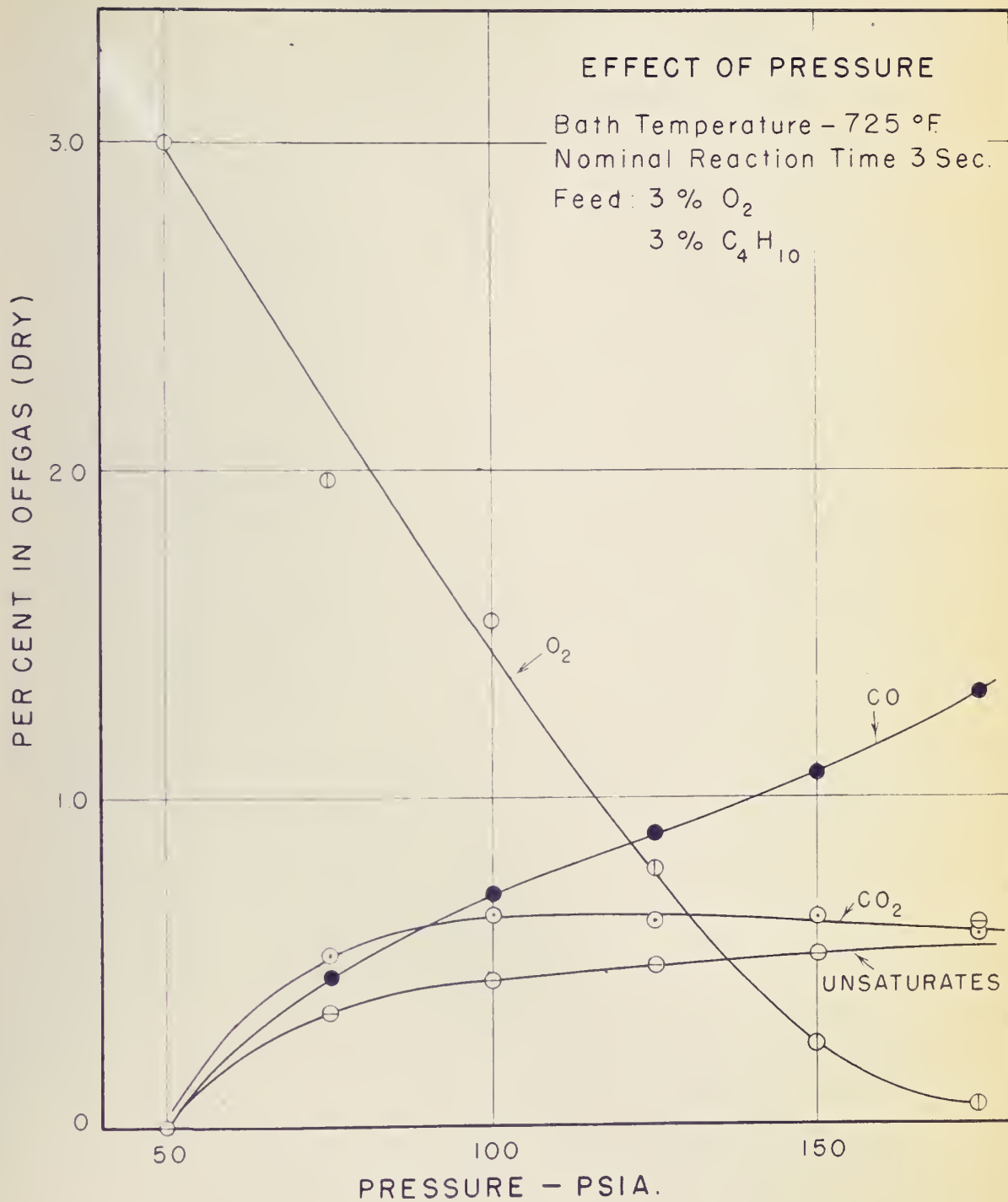
In plotting the useful product yield curves, the mass spectrometer analysis for Run 4-A was ignored because of its incompatibility with the other results. This run was one of four consecutive runs, all of which gave misleading mass spectrometer analyses. The yields of individual useful products pass through a common maximum and then decline in favour of further CO formation. The optimum yield was attained in the vicinity of 130 psia. with a conversion in a single pass of 14 per cent of the total carbon.

After the initial step of the reaction, the oxygen concentration may have been lowered to the point where no further reaction with the useful products occurs. The products themselves appear stable to pyrolysis at the reaction temperatures encountered. This critical oxygen content diminishes as the reaction pressure increases because of the change in partial pressures, in effect, concentration.
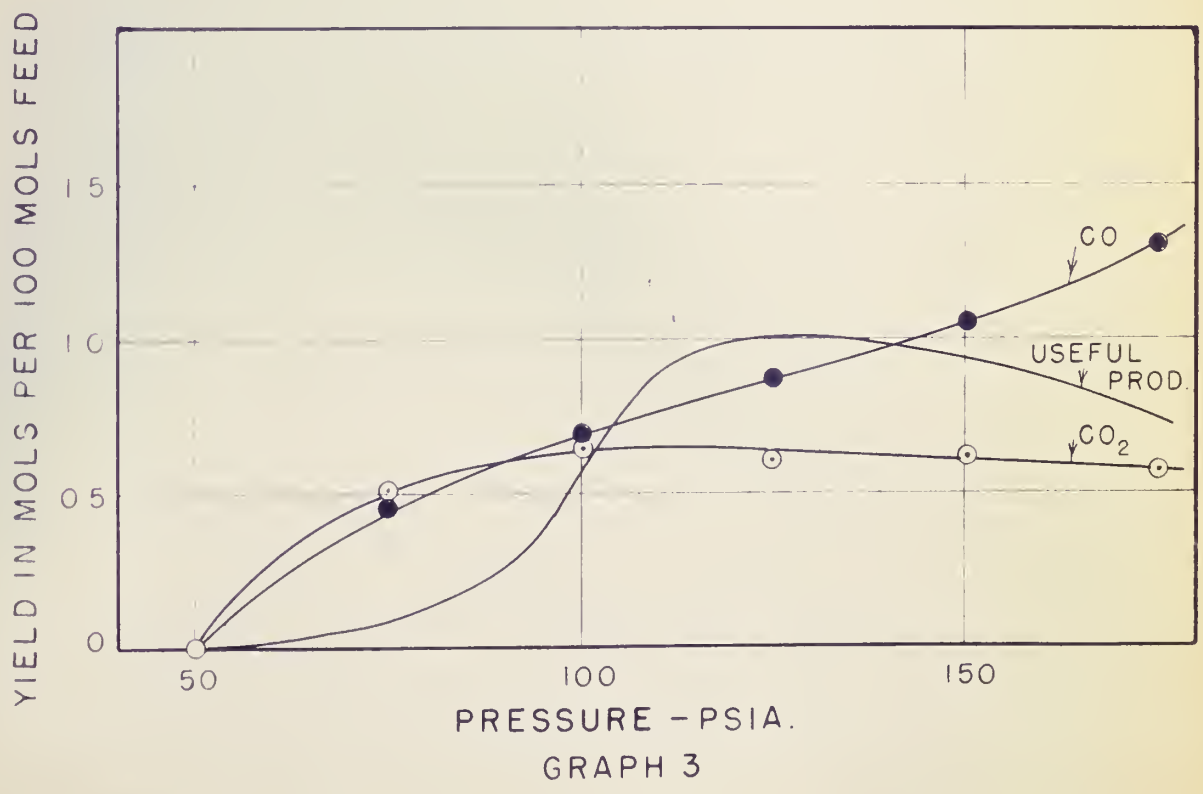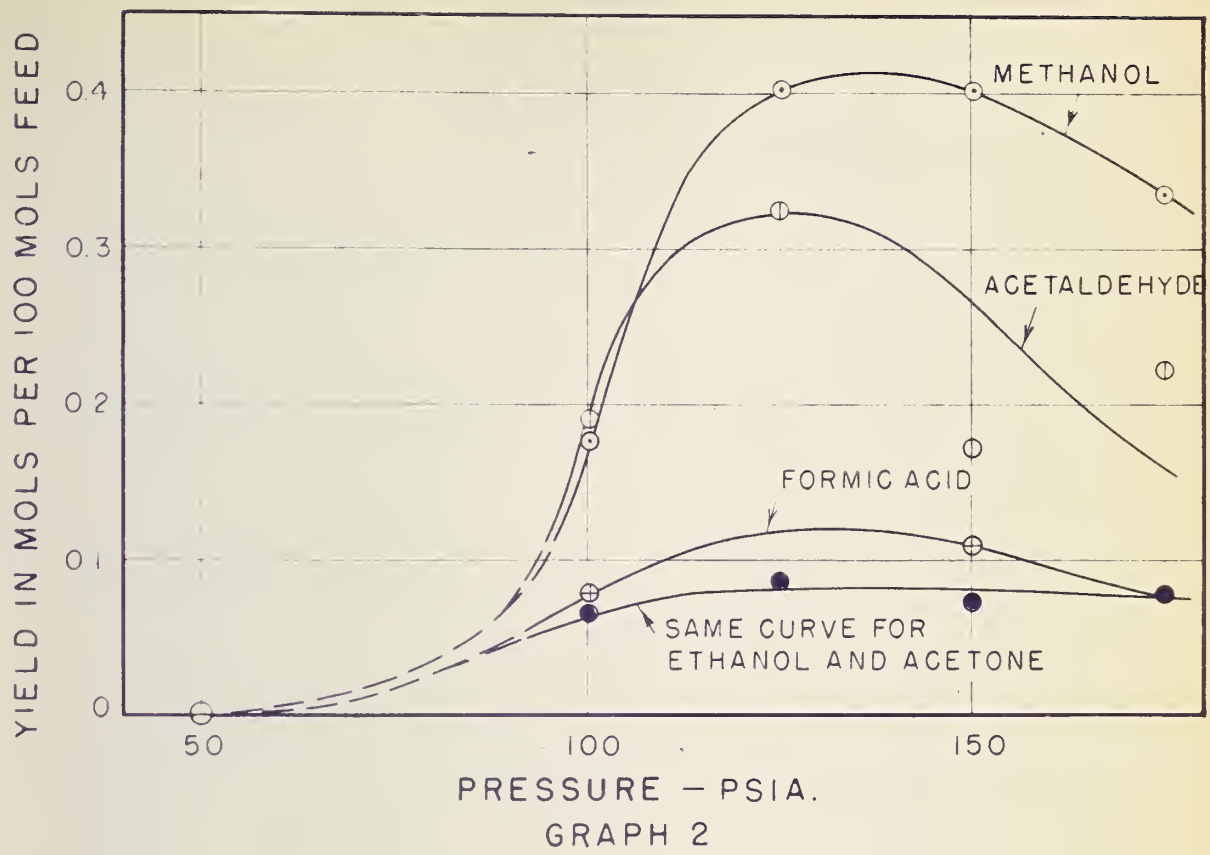
The appearance of unsaturates conforms with the initiation of the reaction and reaches a near maximum quickly after which a gradual increase is shown. This fact alone is not of significance but it may be of assistance in later discussion.

Effect of Reaction Time

These runs were performed at a pressure of 100 psia., bath temperatures of 723 to 726°F and inlet gas composition of three per cent oxygen and three per cent butane. Graphs 6 to 10 and Figure 10 show the effect of varying the reaction time from 1.0 to 4.5 sec.
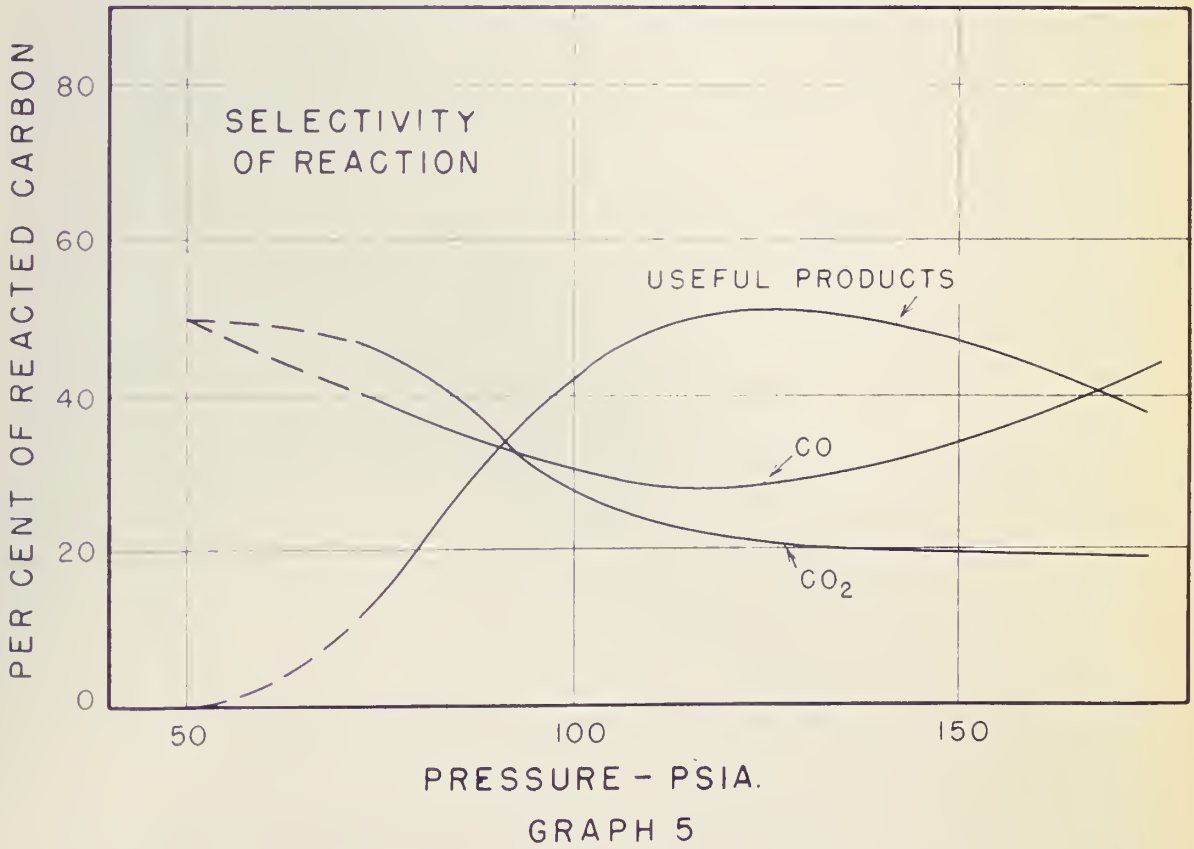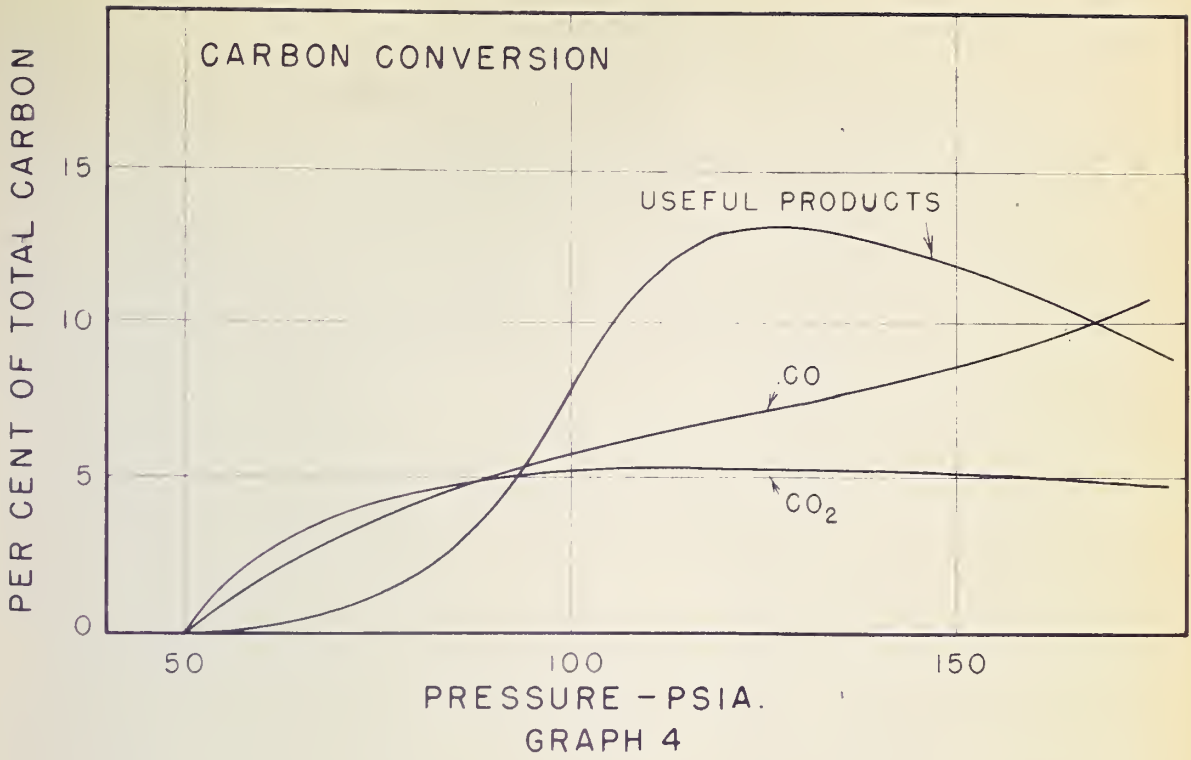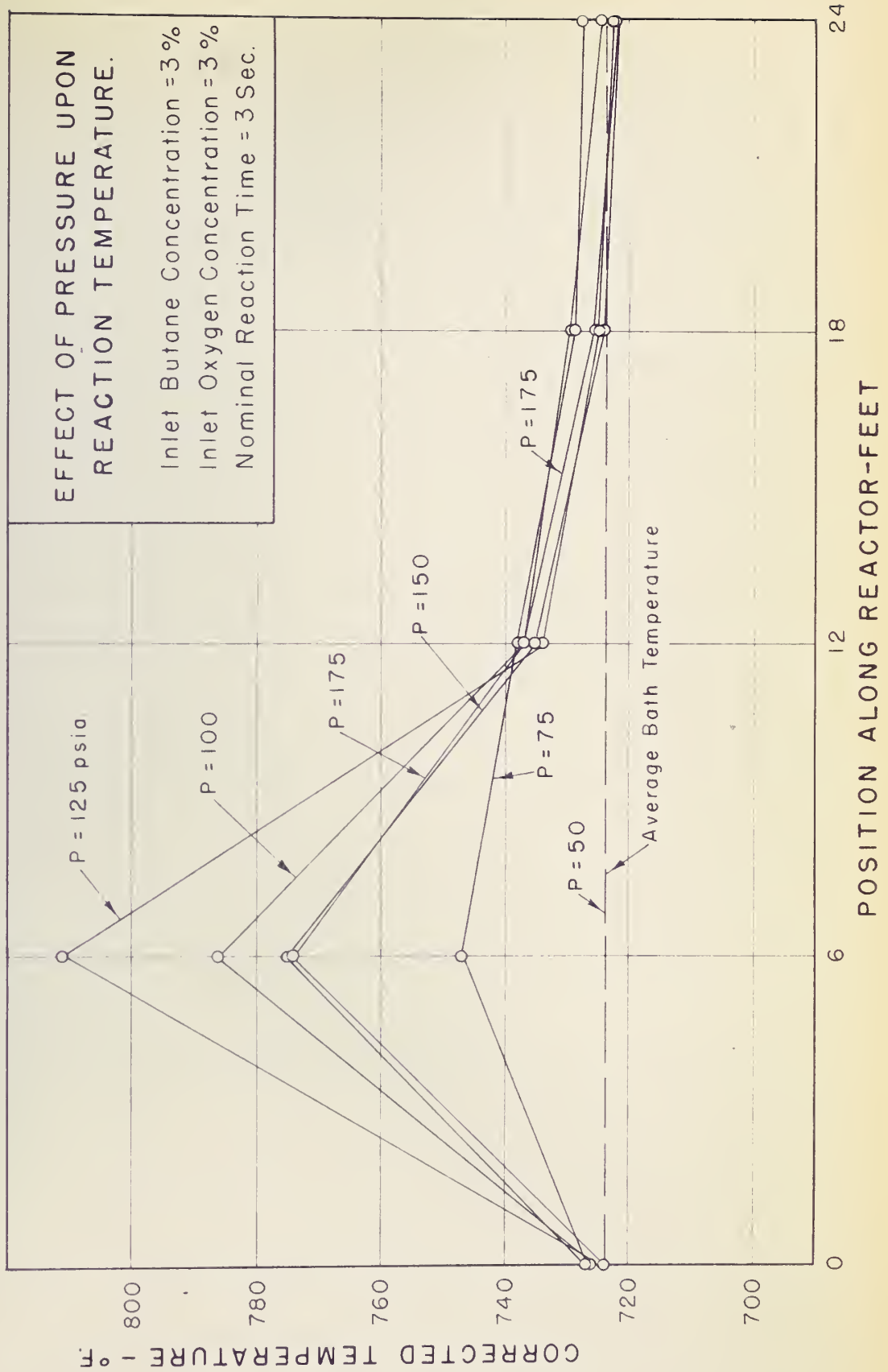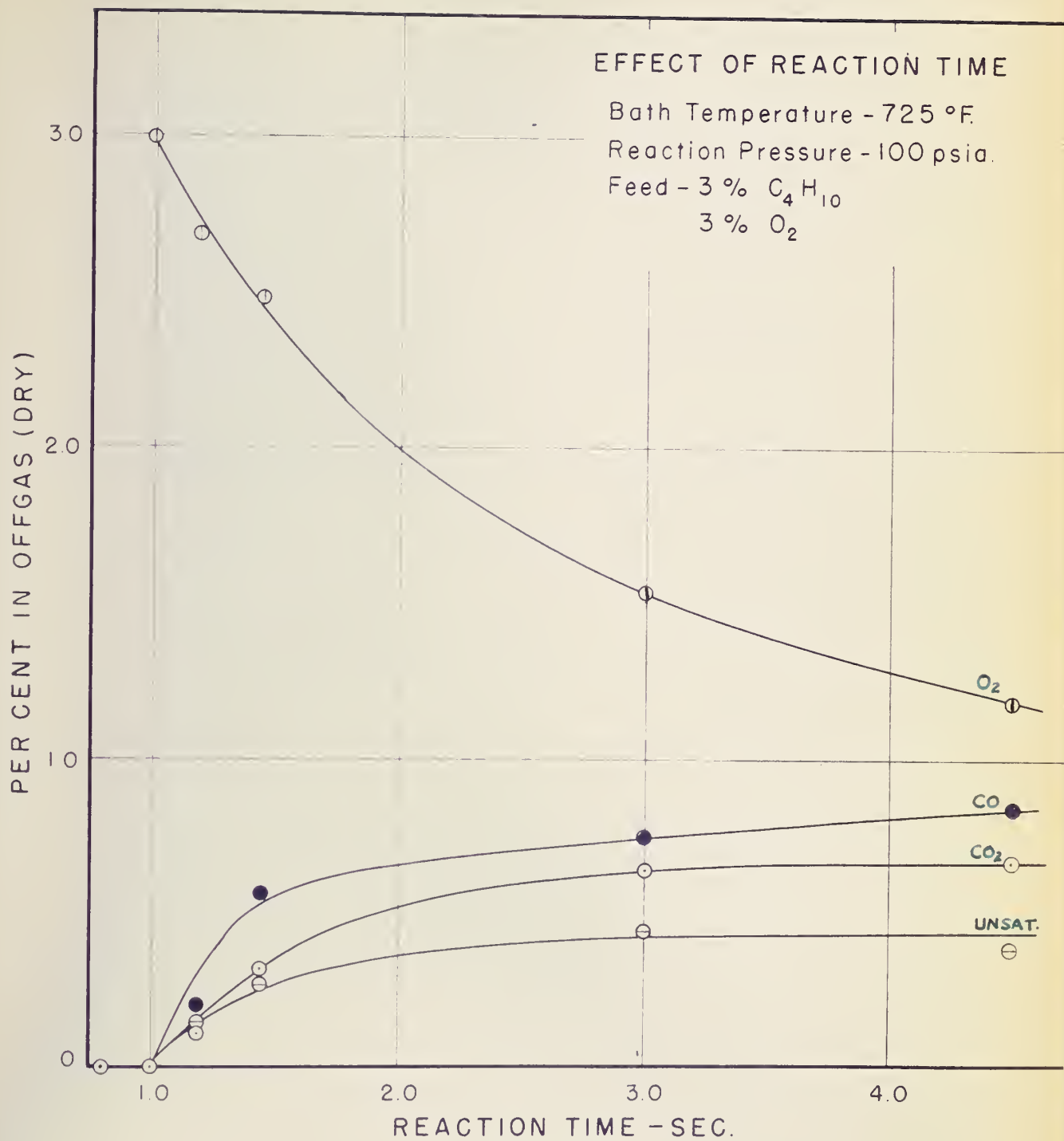
EFFECT OF PRESSURE

Bath Temperature – 725 °F.
Nominal Reaction Time 3 Sec.
Feed: 3 % O_2
       3 % $C_4 H_{10}$

PRESSURE – PSIA.

GRAPH I

GRAPH 2

GRAPH 3

CARBON CONVERSION

PER CENT OF TOTAL CARBON

USEFUL PRODUCTS

CO

CO_2

PRESSURE - PSIA.

GRAPH 4

SELECTIVITY
OF REACTION

PER CENT OF REACTED CARBON

USEFUL PRODUCTS

CO

CO_2

PRESSURE - PSIA.

GRAPH 5

FIGURE 9

EFFECT OF PRESSURE UPON
REACTION TEMPERATURE.

Inlet Butane Concentration = 3%
Inlet Oxygen Concentration = 3%
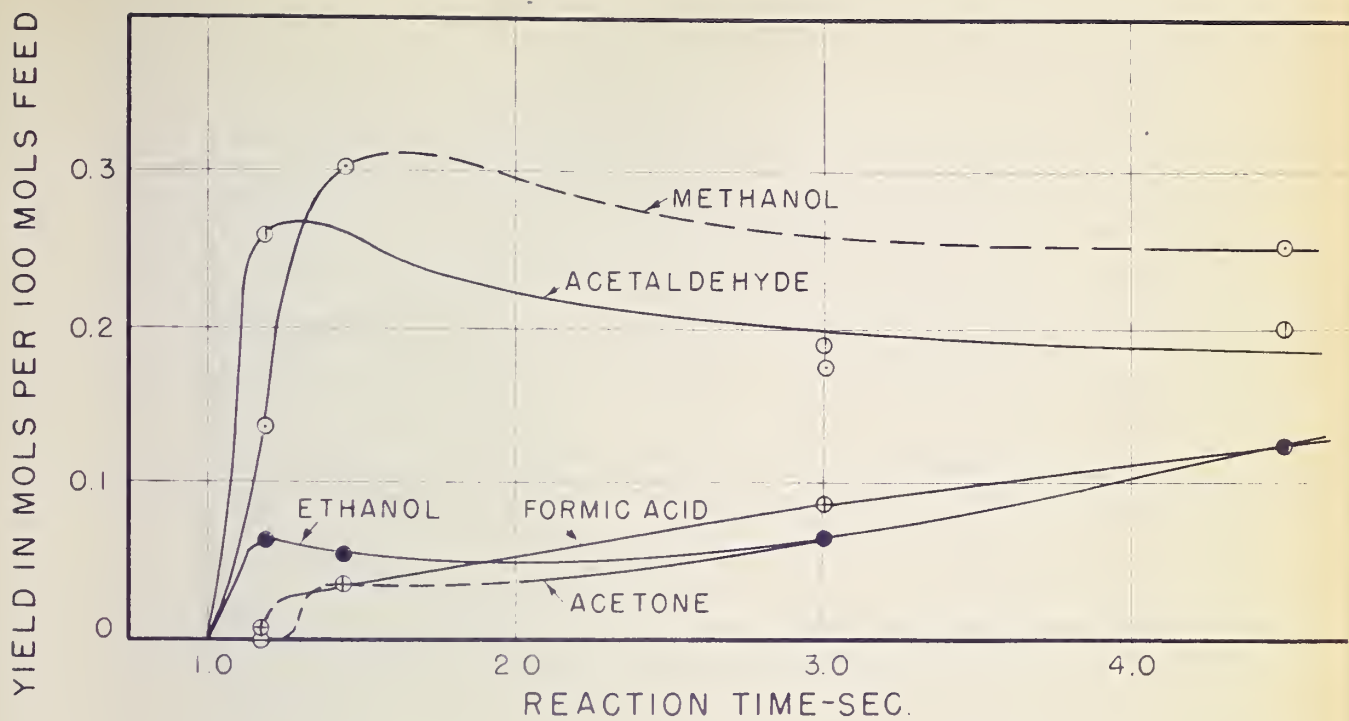Nominal Reaction Time = 3 Sec.

At reaction times of 0.8 and 1.0 sec, no reaction was apparent. The significant effect of reaction time lay in the rapidity of formation of useful products during the interval of 1.0 to 1.5 sec. where they quickly reached their maximum yields in preference to CO_2 and CO formation. The selectivity curve very clearly shows this distinctive feature. Above 1.5 sec, little occurs other than a gradual increase in the oxygen reacting to both useful products and CO. Slight variations in reaction times greater than 2.5 sec.are shown to have negligible effect on the yields because of the low slope of the yield-reaction time curves.

The mass spectrometer analyses indicate early formation of acetaldehyde, ethanol and methanol but the shorter the period the more it is indicated that ethanol and acetaldehyde are the initial oxidation products. Methanol then becomes significant with acetone appearing last. Formic acid yields appear to increase linearly with contact time and the exact point where it appears is not known relative to the other products. The gradual increase in formic acid may be taken as evidence of origin in a secondary reaction, more likely to occur with an increasing reaction temperature.
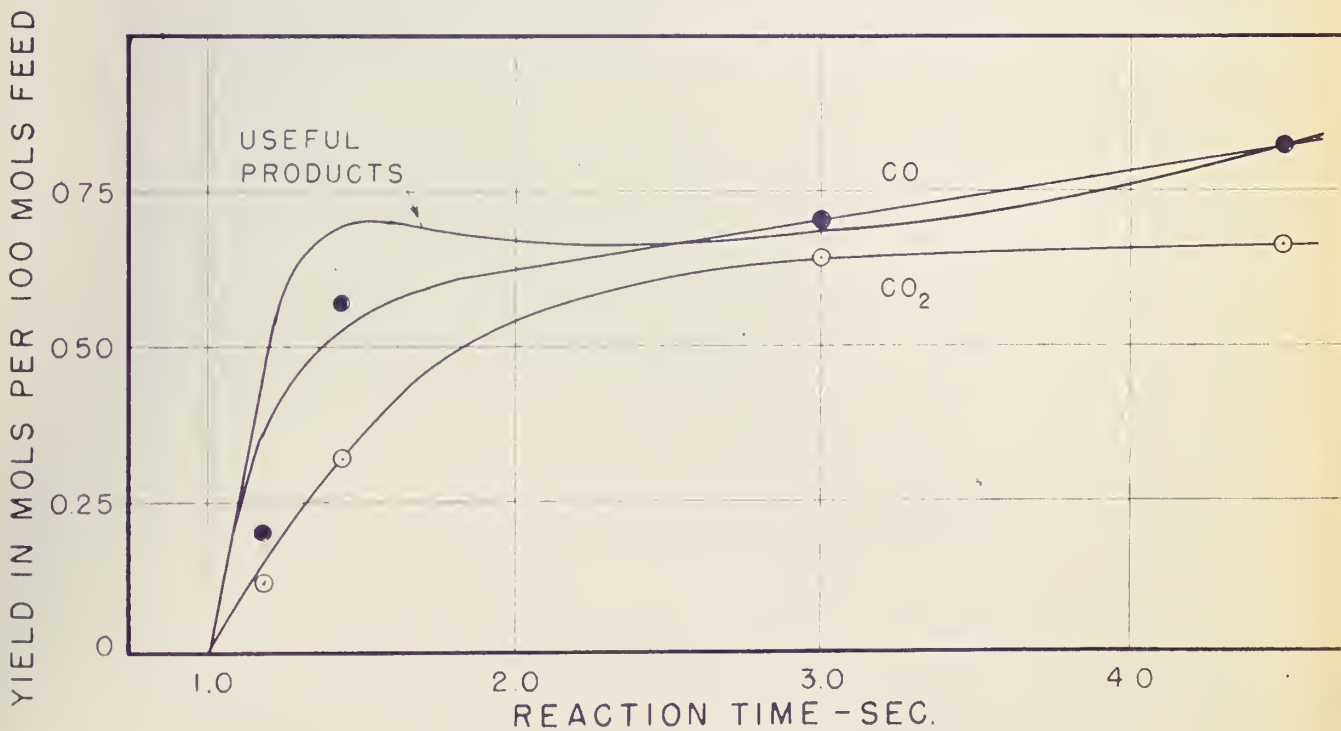
The primary useful products yield curves show a characteristic dip after the early reaction peak. This may be attributed to the thermal influence of the reactor design. The longer the reaction time, the higher the reaction temperature which was attained because temperature rise suppression by reactor cooling would be least at low mass velocities. The lower temperatures between 1.0 to 1.5 sec runs would favour increased yields of useful products which in turn decrease as the reaction temperature
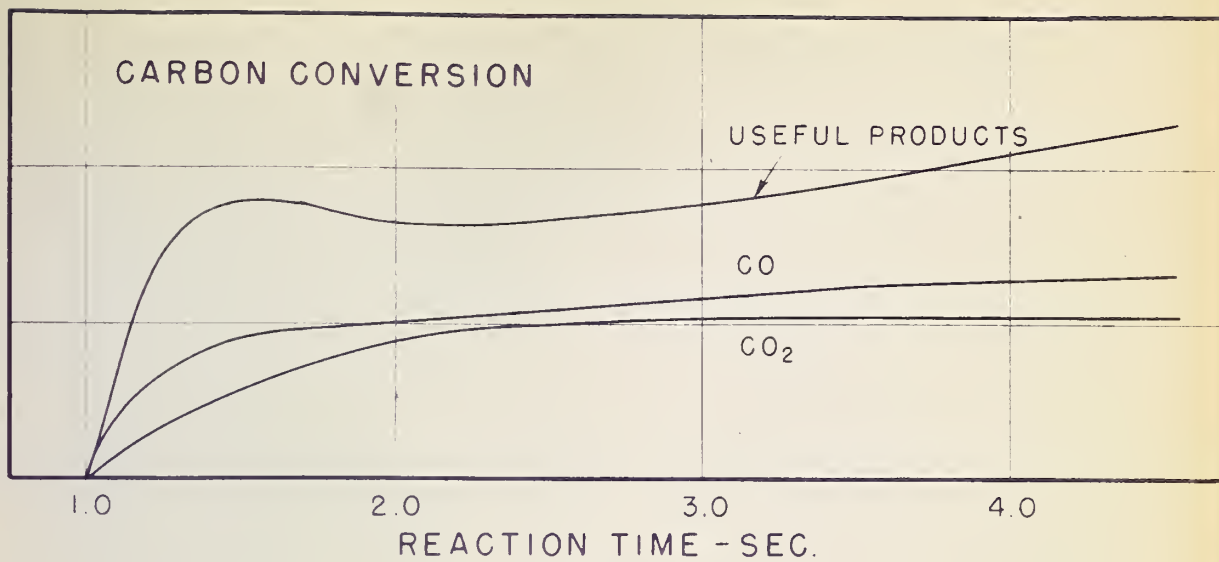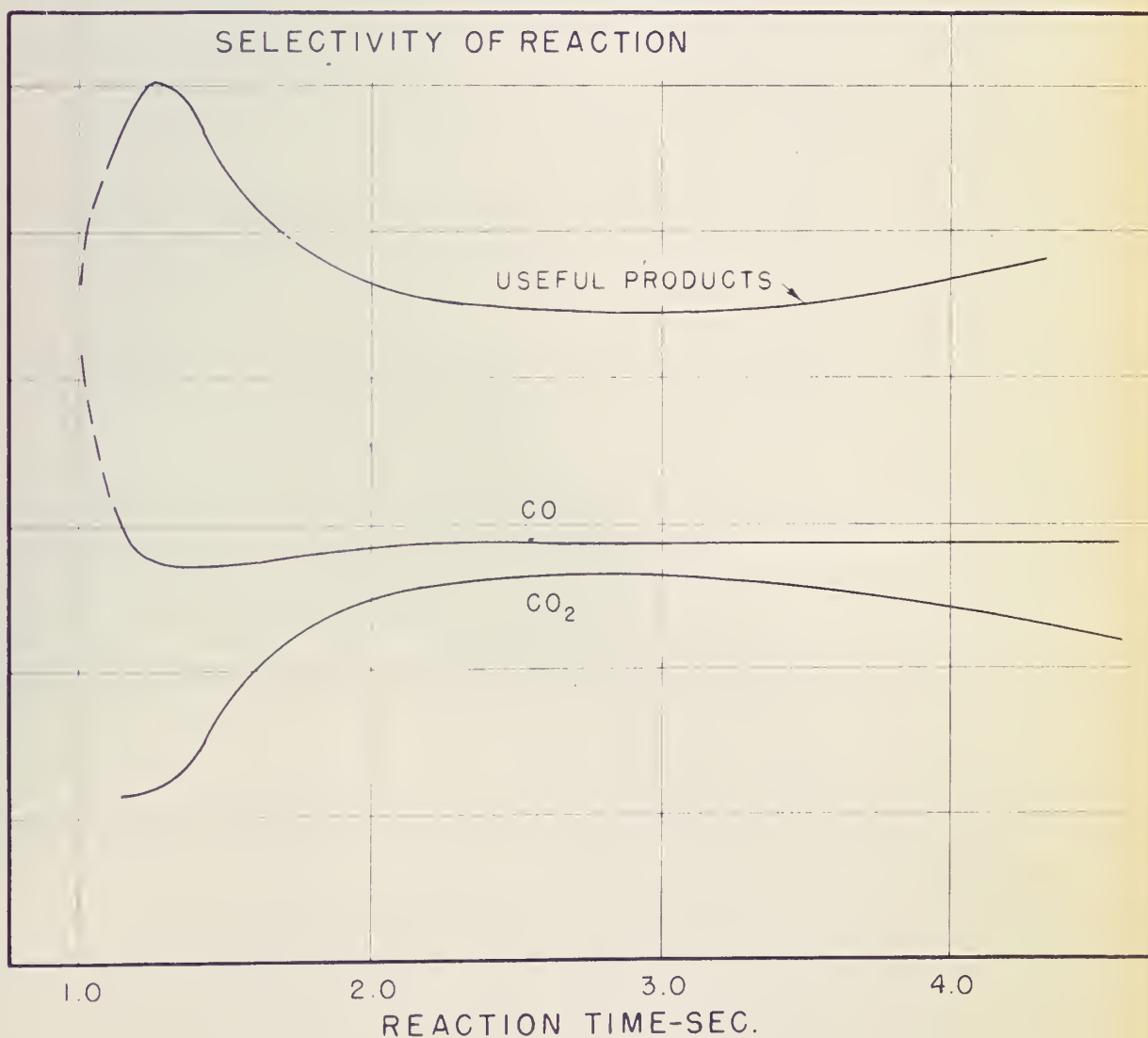
EFFECT OF REACTION TIME

Bath Temperature - 725 °F.
Reaction Pressure - 100 psia.
Feed - 3 % C_4H_{10}
     3 % O_2

PER CENT IN OFFGAS (DRY)

O_2

CO

CO_2

UNSAT.

REACTION TIME - SEC.

GRAPH 6

GRAPH 7

GRAPH 8

CARBON CONVERSION

USEFUL PRODUCTS

CO

CO$_2$

REACTION TIME - SEC.

GRAPH 9

SELECTIVITY OF REACTION

USEFUL PRODUCTS

CO

CO$_2$

REACTION TIME-SEC.

GRAPH 10

FIGURE 10.

EFFECT OF REACTION TIME
UPON REACTION TEMPERATURE

Reaction Pressure = 100 psia.
Inlet Butane Concentration = 3%
Inlet Oxygen Concentration = 3%
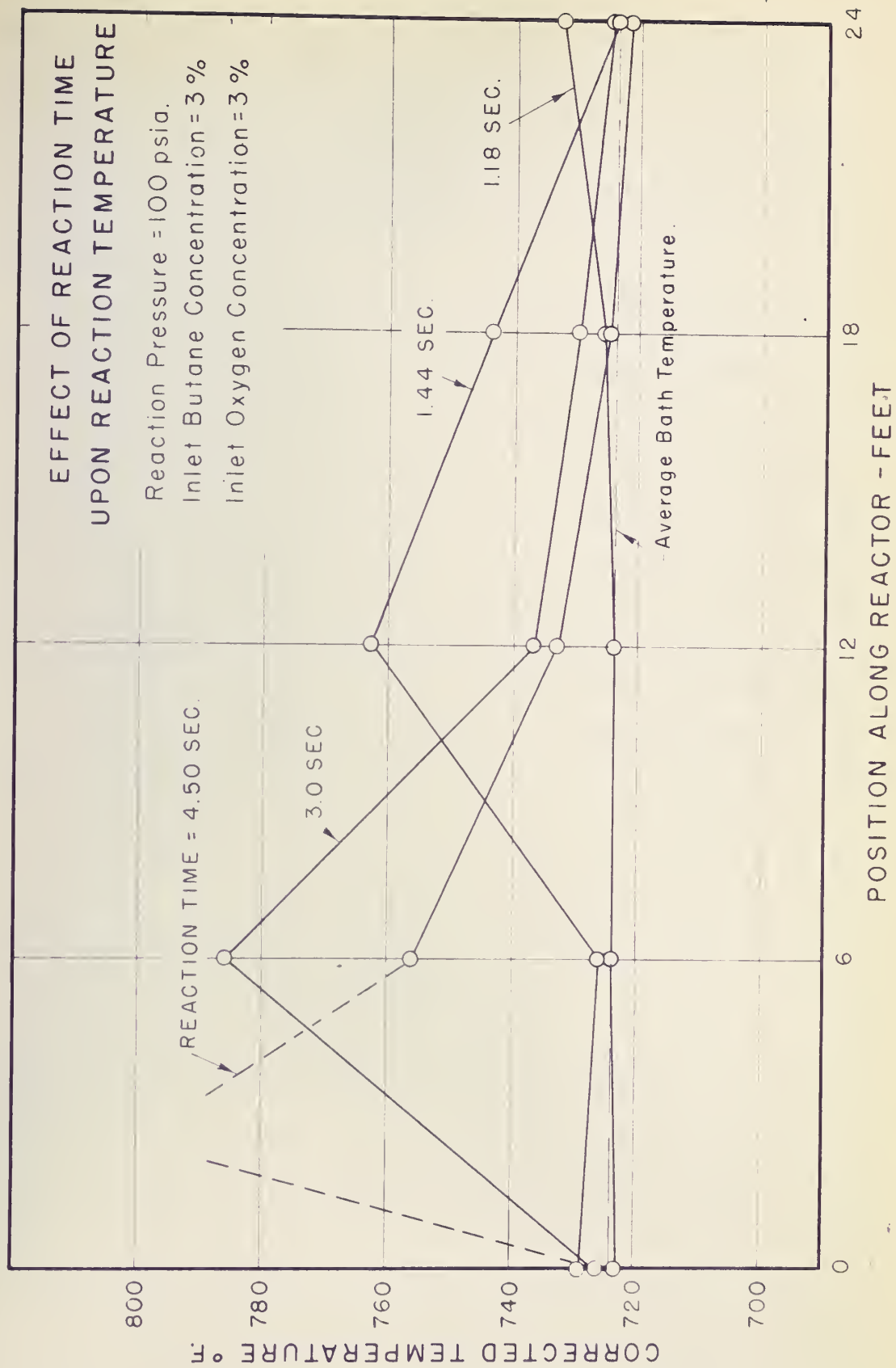
increases. The more stable intermediates such as formic acid and
acetone would increase slightly because their formation may be
accelerated with increasing temperatures. The yield-reaction time
curves are not truly comparable because each run was subject to a
differing thermal influence.

The temperature profiles indicate a characteristic surge
shortly after the initiation of the reaction followed by a short
period in which the reaction is essentially completed and lastly,
cooling of the gases to the bath temperature. Very definite evidence
of an induction period is shown by the profiles. Although the reaction
times are nominal and subject to some error, the following induction
period may be deduced on the basis of the calculated reaction times:

Considering the section in which the reaction first appeared

Run	Time in sec/section	Induction period, sec.
4.50 sec.	1.13	0.56 ± 0.56
3.0	0.75	0.75 ± 0.75
1.44	0.36	0.72 ± 0.36
1.18	0.29	0.73 ± 0.15

Average induction time 0.72 $+0.18 \atop -0.13$

This induction period is an average for these runs subject to perhaps
10 per cent error and assumes the induction period to be independent
of the mixing between the feed junction and the point of reaction
initiation.

The use of reaction time rather than space velocity as the
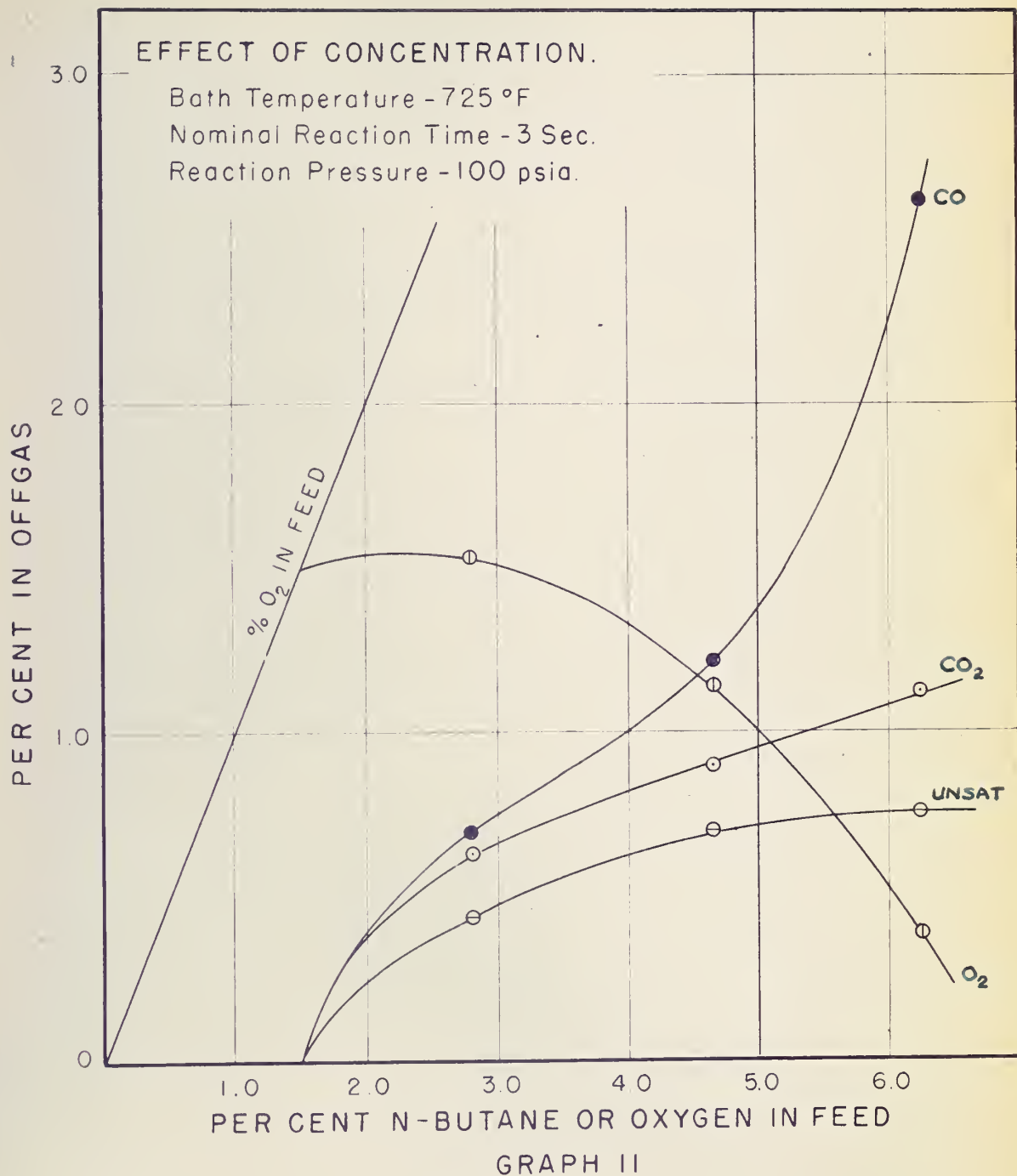basis for plotting this data may be questionable. The justification

for this approach lies in the fact that because of the large inert content of the feed stream, the fractional molar change is small and hence both space velocities and reaction times may be used. The latter gives a better physical picture and is more useful from a kinetic viewpoint.
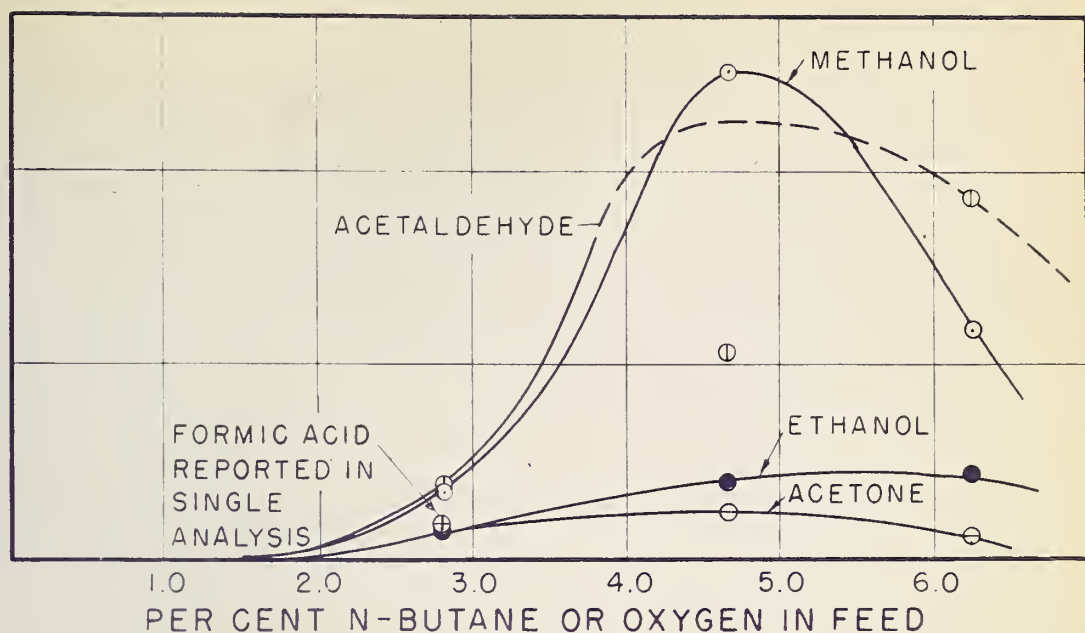
Effect of Concentration

These runs were performed at a pressure of 100 p.s.i.a., reaction time of 3.0 sec., butane to oxygen feed ratio of one and bath temperatures of 724 to 727°F. Graphs 11 to 15 and Figure 11 were plotted from the data.

At 1.5 per cent oxygen (and 1.5 per cent butane), traces of reaction occurred but the product yields were too small for accurate determination. This value was taken as the minimum concentration for reaction initiation. Upon increasing the oxygen-butane concentration, the reactivity of the mixture increased steadily until 4.0 per cent was reached after which the conditions were so severe as to tend to force the oxidation towards completion. This is shown by the exponential increase in H_2O and CO produced. The heats of reaction paralleled this exponential increase.

Temperature profiles for runs up to 4.5 per cent oxygen (and 4.5 per cent butane) were similar to other profiles but when these values were raised to 6.0 per cent, the temperature at the 6-ft. mark in the reactor was considerably lower than for the other runs. However, the heat of reaction was very high; hence there must have been a high temperature at some other point in the reactor.
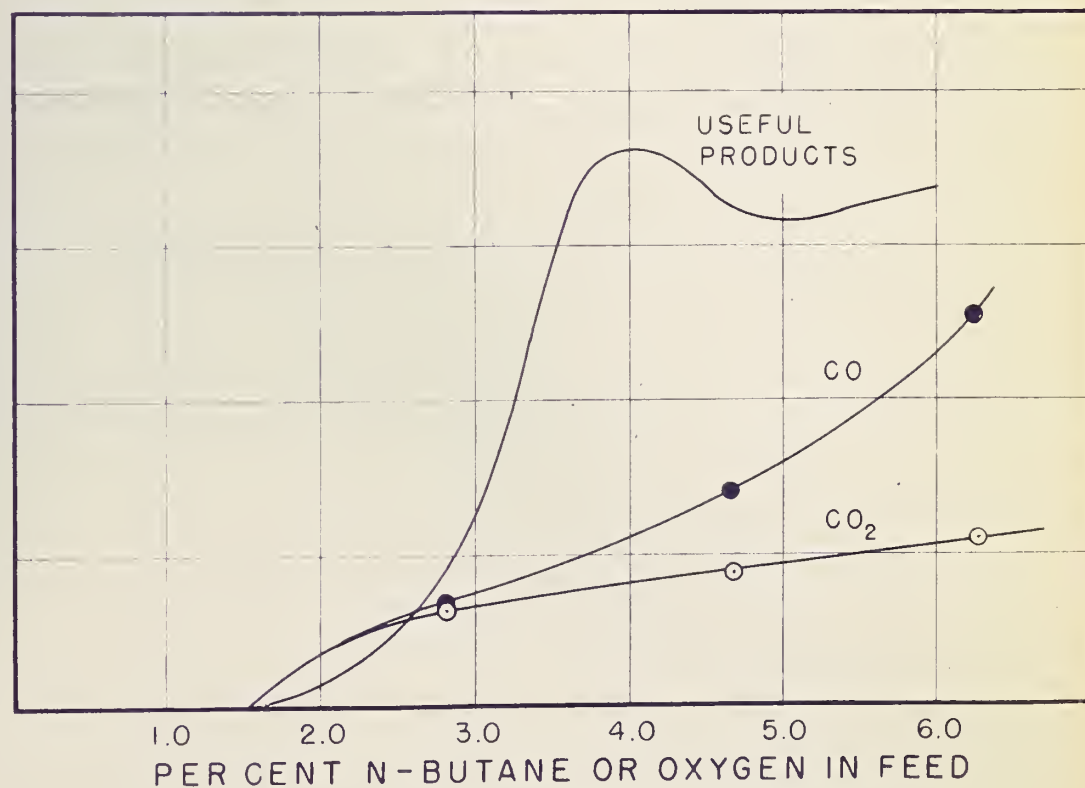
EFFECT OF CONCENTRATION.

Bath Temperature – 725 °F
Nominal Reaction Time – 3 Sec.
Reaction Pressure – 100 psia.

% O_2 IN FEED

CO

CO_2

UNSAT

O_2

PER CENT IN OFFGAS

PER CENT N–BUTANE OR OXYGEN IN FEED

GRAPH II

GRAPH 12

GRAPH 13

CARBON CONVERSION

PER CENT OF TOTAL CARBON

USEFUL PRODUCTS

CO

CO_2

PER CENT N-BUTANE OR OXYGEN IN FEED

GRAPH 14

SELECTIVITY OF REACTION

PER CENT OF REACTED CARBON

USEFUL PRODUCTS

CO

CO_2

PER CENT N-BUTANE OR OXYGEN IN FEED

GRAPH 15

FIGURE II

EFFECT OF CONCENTRATION
UPON REACTION TEMPERATURE

Reaction Pressure = 100 psia.
Nominal Reaction Time = 3 Sec.
Inlet Butane-Oxygen Mol.
Ratio is 1:1
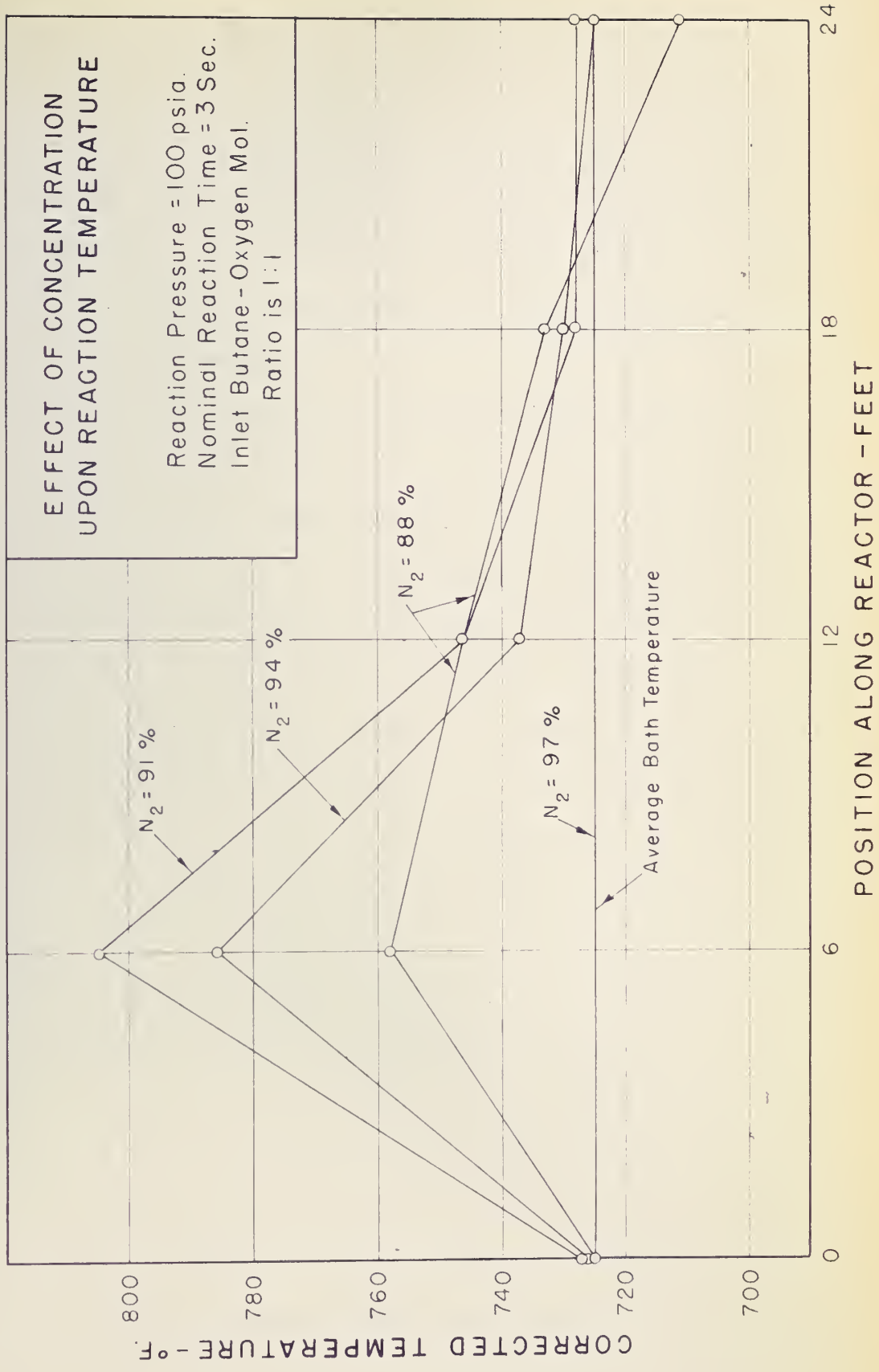
The reaction time for this run was slightly larger than 3.0 sec. and as a result, the reaction peak must have been displaced towards the inlet. The temperature at the 12-ft. mark appears high relative to · other runs indicating more reaction between the 6-ft. and 12-ft. marks. This prolonged reaction at 100 psia. with a final offgas composition of greater than four per cent butane and 0.39 per cent oxygen appears contradictory to the earlier runs.

The useful product yield curves, taking methanol as being representative, swing through a maximum at approximately 4.0 per cent O_2 or C_4H_{10}. The yields then decline because of the highly increased reaction temperatures leading to the decomposition of the intermediates. Ethanol and acetone both appear more resistant to further oxidation than methanol. Acetaldehyde yields are obscured because of loss of sample during the 4.6 per cent run. Formic acid was not reported quantitatively for all of these analyses but its presence under these conditions certainly appears likely. Conversion of total carbon to useful products could be expected to exceed 20 per cent at four per cent oxygen or butane.

Effect of Butane

Butane concentration studies were carried out at a pressure of 100 psia. reaction time of 3.0 sec. and oxygen concentration of three per cent. Bath temperatures ranged from 723 to 730°F. Run B-6 was included in this series although the oxygen concentration was 3.6 per cent because the butane-oxygen ratio was felt to be significant. No other corrections were applied to B-6 to offset the increased yields. Graphs 16 to 20 and Figure 11 show the effect of butane.

The minimum butane required for initiation of the reaction could not be determined but from the slope of the yield curves it is indicated as being very low. The curves were plotted through the origin indicating any concentration would react. If a minimum oxygen concentration only is considered necessary to chain initiation, then with three per cent oxygen, reaction would take place with butane at any concentration. Most oxidation theories propose an oxygen molecule, atom or oxygenated radical as the chain initiator. Within this reactor, any run made with three per cent oxygen in the feed and a pressure of 100 psia. resulted in reaction after the induction period. For this reason, the concentration of three per cent oxygen appears above the critical concentration for chain propagation.
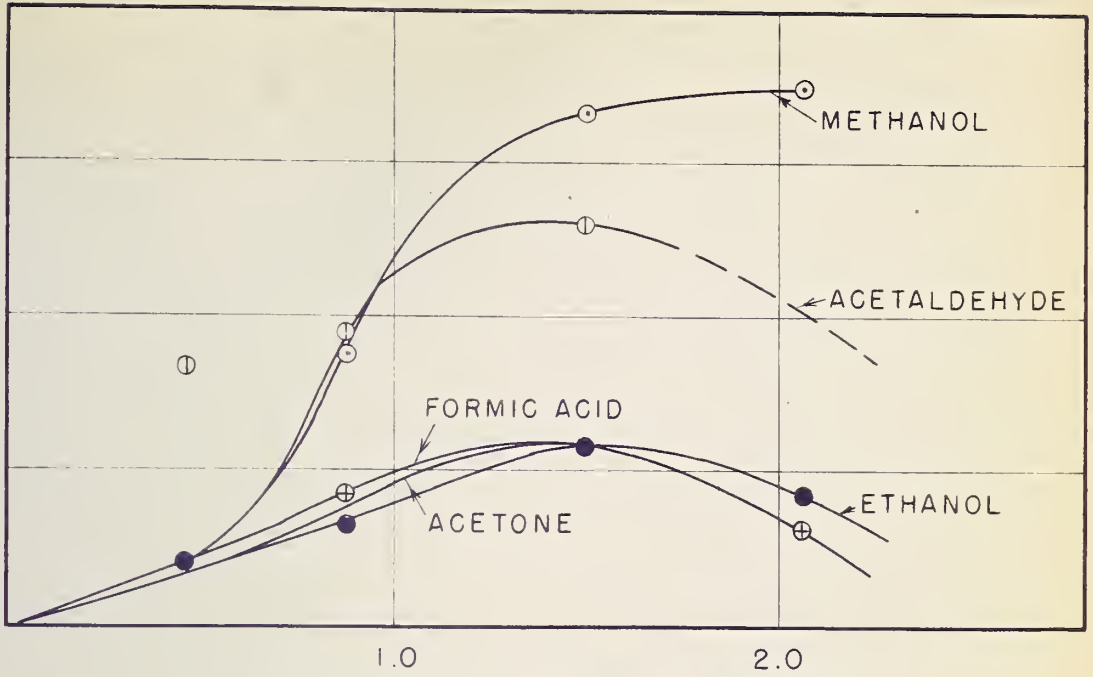
Considerable scatter in the offgas analyses is evident, particularly for CO: consequently the accuracy of the yields is questionable. With increased butane concentration, both heats of reaction and reaction temperature increased. The increased temperatures to some extent are responsible for the peak in the useful products yield curve. With butane concentrations above three per cent, increases in carbon conversion were not very significant. The selectivity of the reaction also favoured CO and CO_2 in the range three to six per cent butane. The maximum carbon conversion to useful products reached 10 per cent at a butane to oxygen feed ratio of one to one.

The unsaturates in the offgas increase almost linearly with the increase of butane concentration in the feed. In all other series of runs, a limiting concentration of unsaturates in the offgas was

EFFECT OF BUTANE CONCENTRATION

Reaction Pressure 100 psia.
Bath Temperature – 725 °F.
Nominal Reaction Time – 3 Sec.
Feed – 3 % O_2

CO

UNSATURATES

CO_2

O_2

PER CENT IN OFFGAS (DRY)
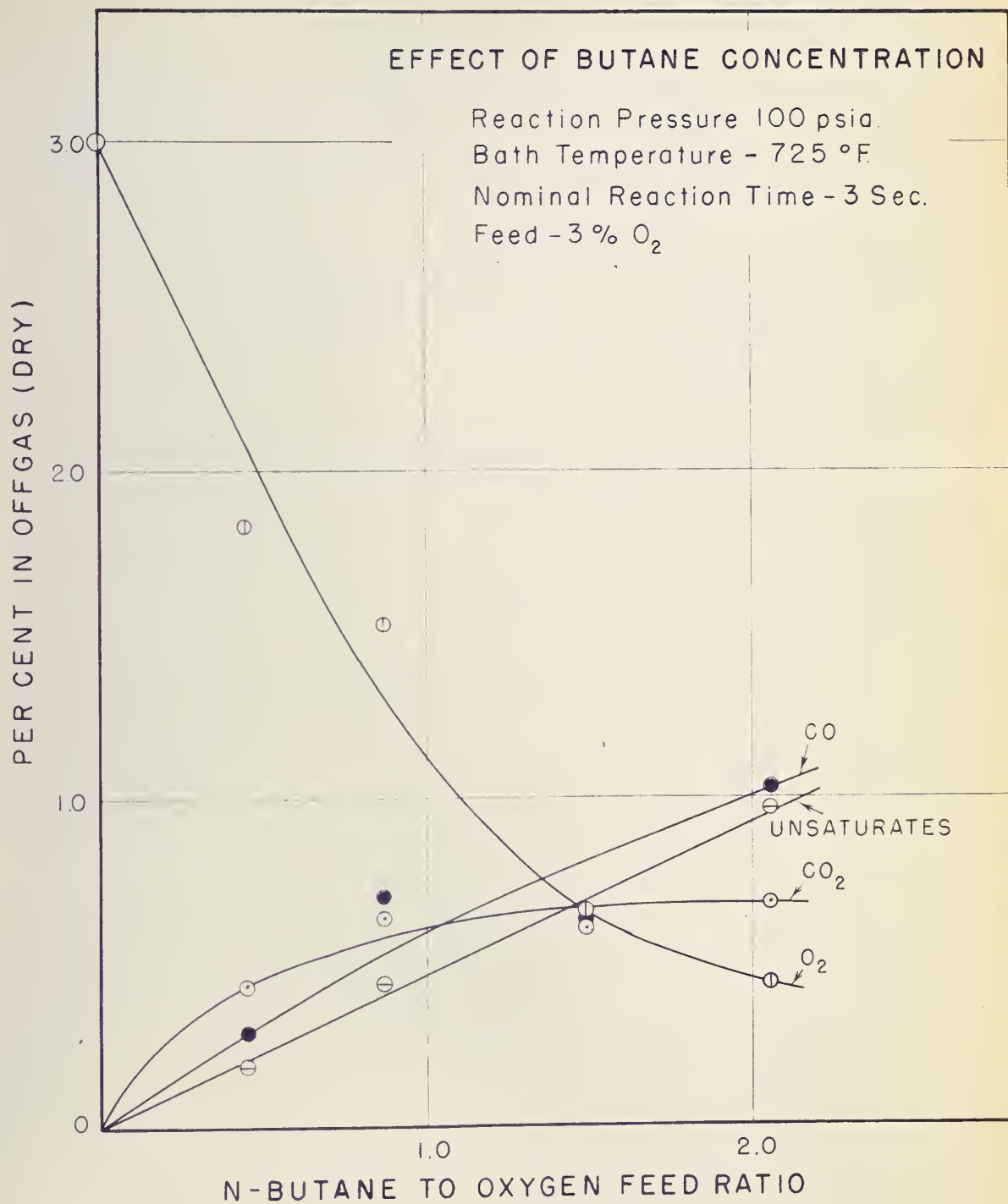
N-BUTANE TO OXYGEN FEED RATIO

GRAPH 16

GRAPH 17

GRAPH 18

CARBON CONVERSION

GRAPH 19

SELECTIVITY OF REACTION

GRAPH 20

- 74 -

FIGURE 12

EFFECT OF VARYING BUTANE CONCENTRATION UPON REACTION TEMPERATURE.

Reaction Pressure = 100 psia
Nominal Reaction Time = 3 Sec.
Inlet Oxygen Concentration = 3%

reached. The origin of the unsaturates may involve an oxygen reaction with the butane and the yield of unsaturates appears proportional to the butane concentration which could indicate a reaction of first order. It is also possible that the greater part of the unsaturates produced may result 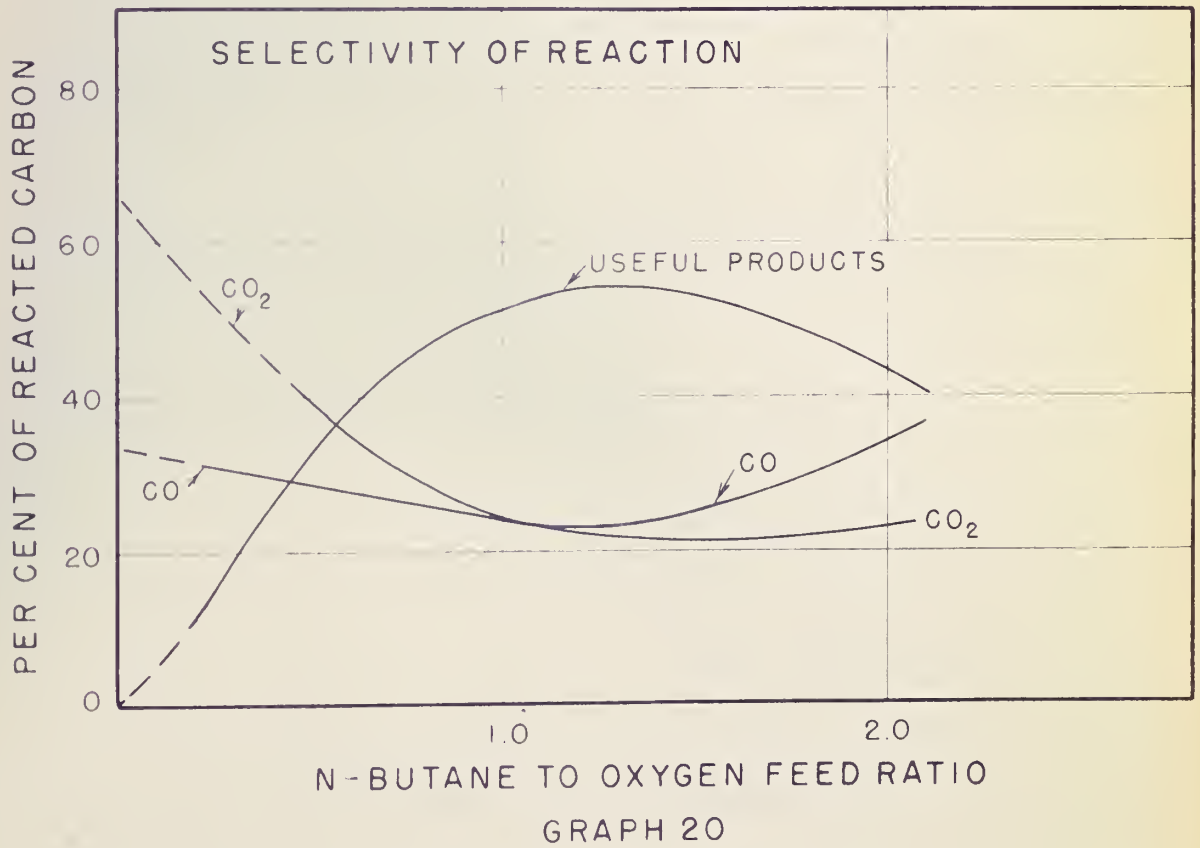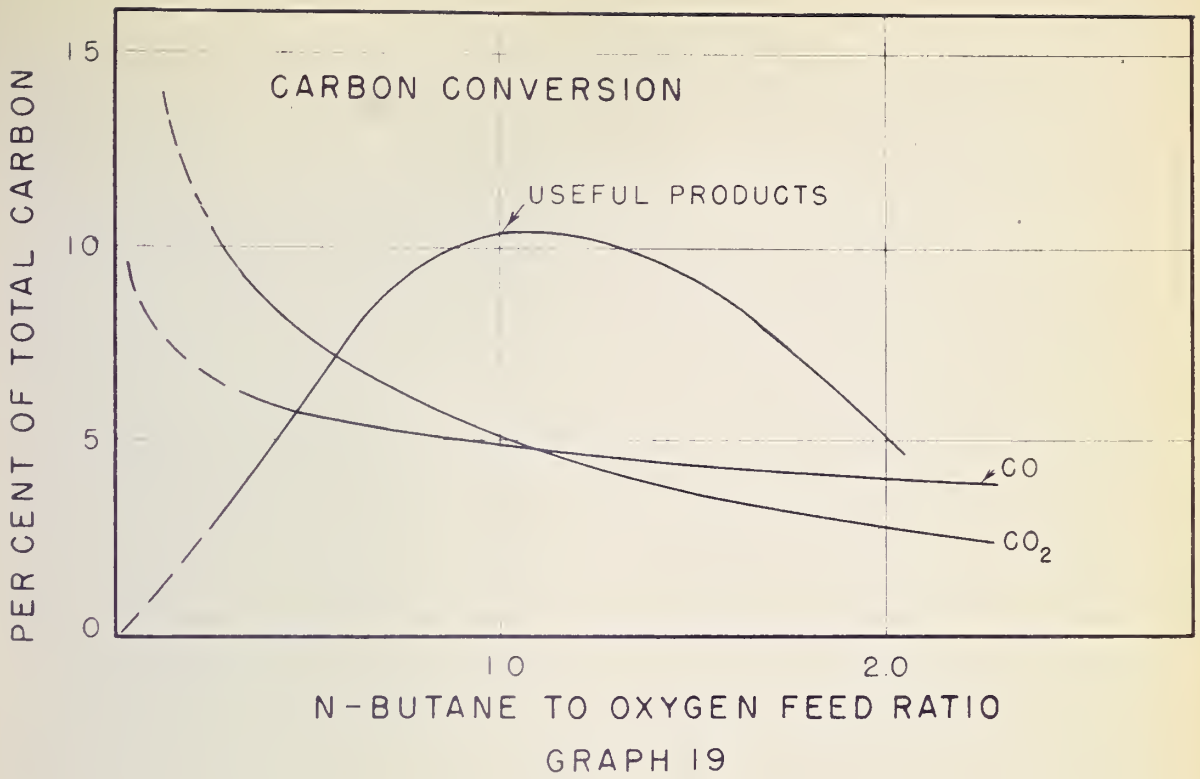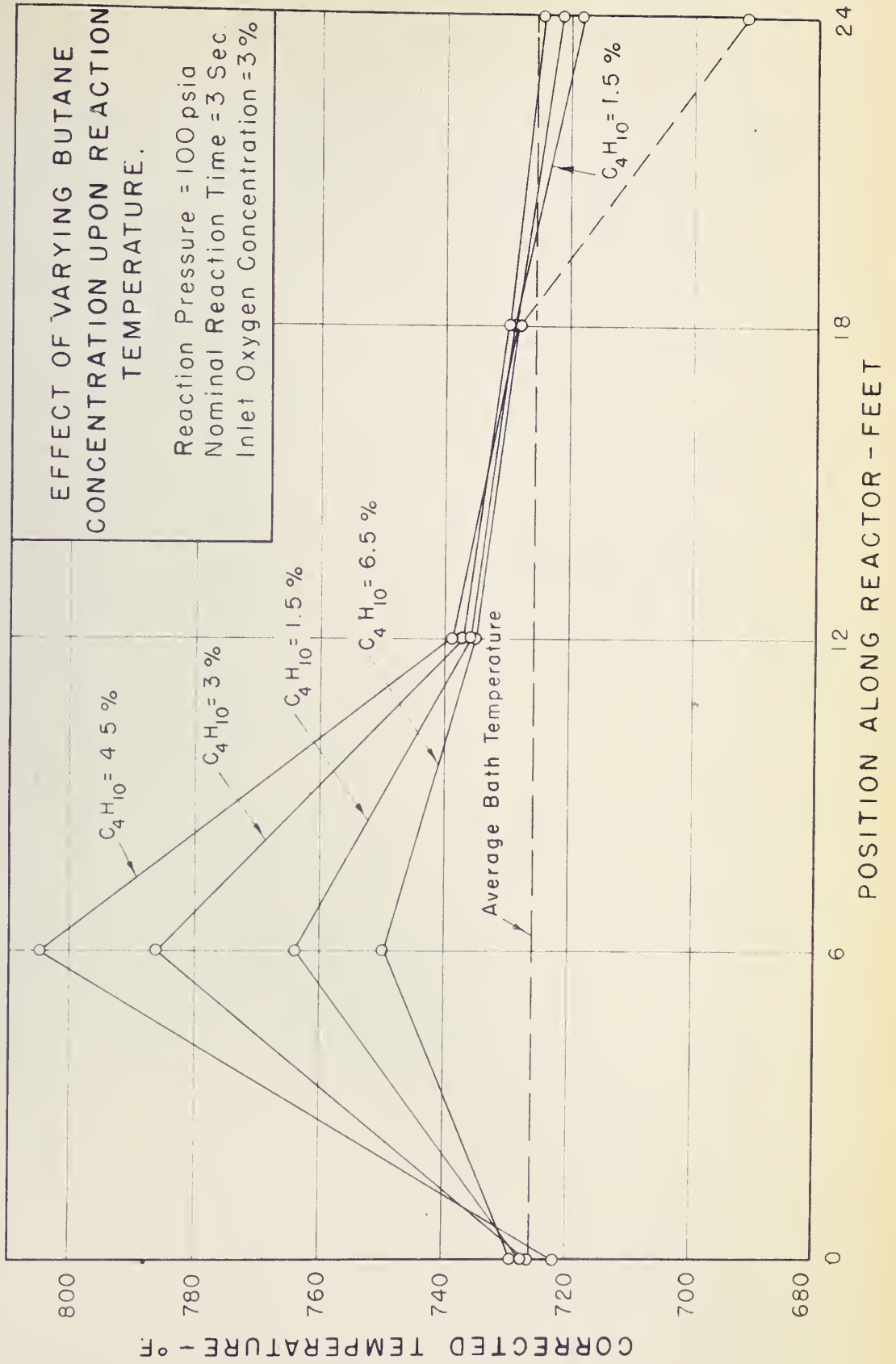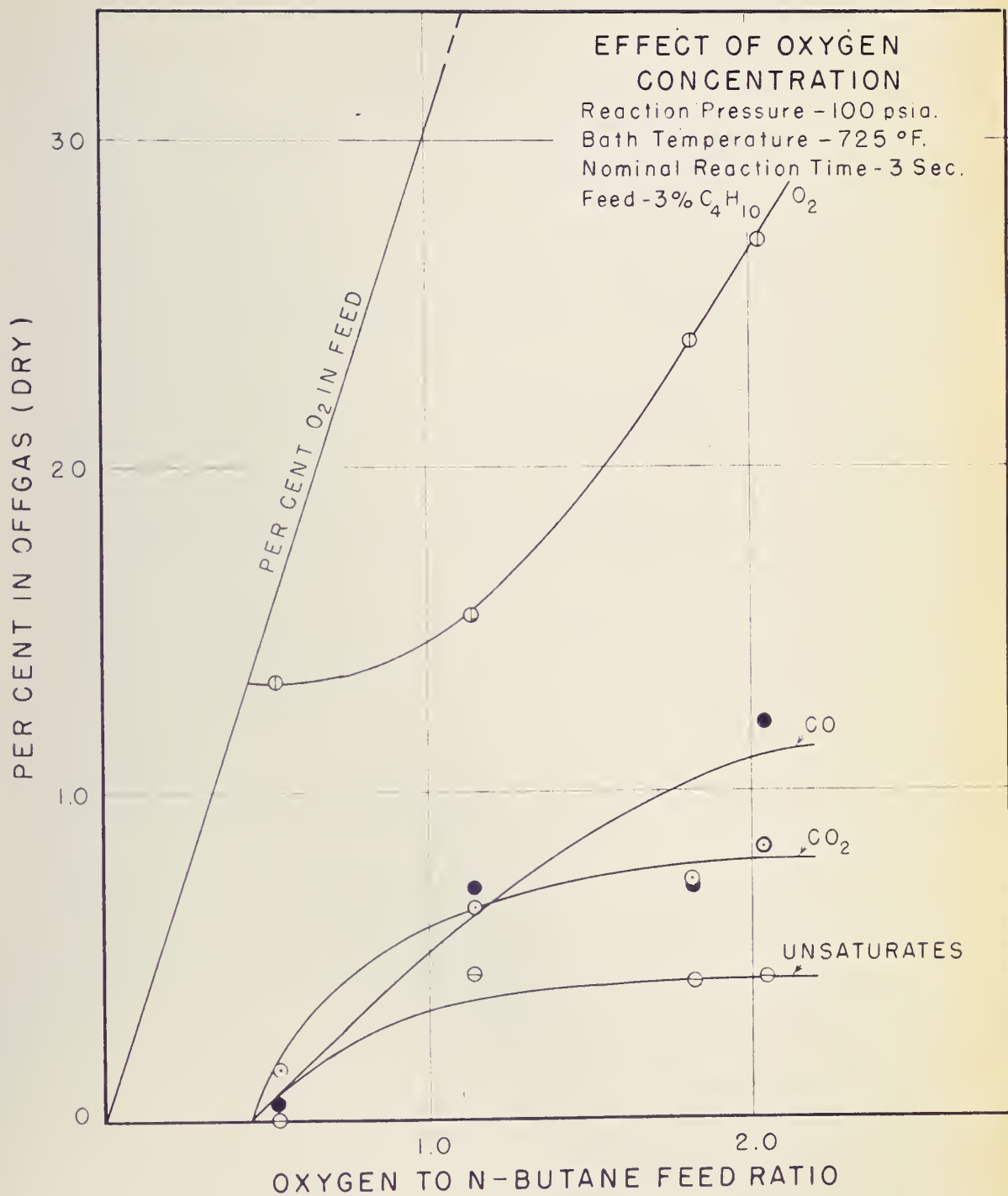from a reaction independent of those which produce the oxygenated carbon compounds. It is unlikely that any unsaturates formed, mainly ethylene, would be subject to further oxidation or reaction because they would be more resistant to further attack.

The temperature profiles again conform in showing increased peaks for increased heats of reaction. An exception arises in the profile for Run B-6. Although butane concentration exceeded seven per cent and excess butane may depress the reaction, the peak has shifted towards the reactor inlet. The explanation may lie in the increased reaction time of 3.4 sec. for this run.

Effect of Oxygen

The effect of oxygen concentration upon butane oxidation has not been clearly established. The data are subject to criticism because the bath temperatures are variant and two of the four mass spectrometer analyses appear incompatible with the material balances for those runs. All runs were made with approximately 2.7 per cent butane in the feed, at a reaction pressure of 100 psia. and reaction time of 3.0 sec., but bath temperatures varied from 712 to 733°F. Graphs 21 to 25 and Figure 13 show the results of these experiments.

With 1.5 per cent oxygen, very little reaction occurred. The data though scattered indicate a minimum concentration of oxygen must be attained before three per cent butane will react.

EFFECT OF OXYGEN
CONCENTRATION
Reaction Pressure – 100 psia.
Bath Temperature – 725 °F.
Nominal Reaction Time – 3 Sec.
Feed – 3% C_4H_{10} / O_2

PER CENT O_2 IN FEED

CO

CO_2

UNSATURATES

PER CENT IN OFFGAS (DRY)

OXYGEN TO N–BUTANE FEED RATIO

GRAPH 21

YIELD IN MOLS PER 100 MOLS FEED

FORMIC ACID
METHANOL
ACETALDEHYDE
SAME FOR
ACETONE
AND ETHANOL

OXYGEN TO N-BUTANE FEED RATIO
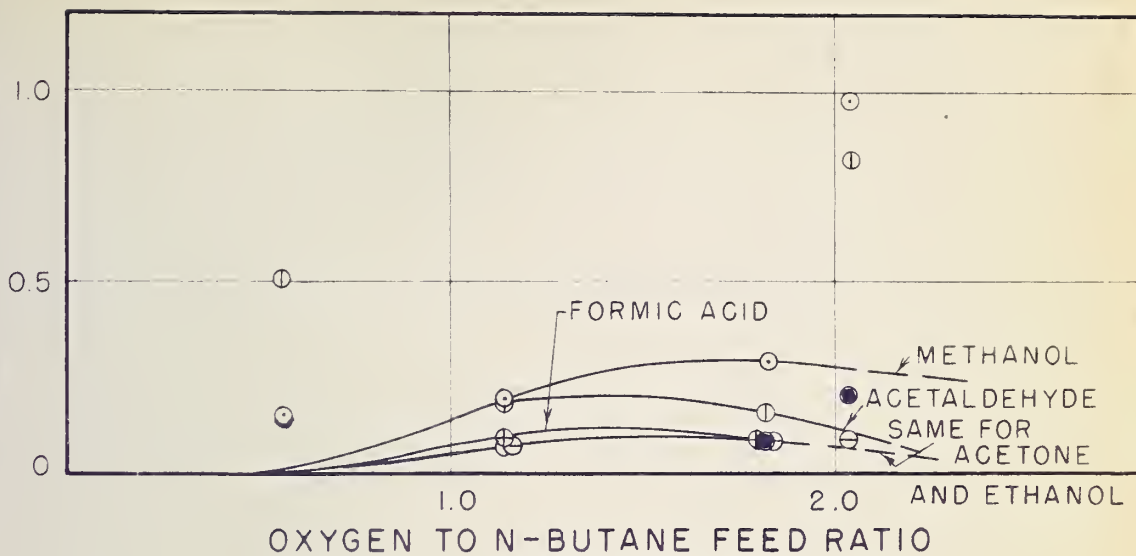
GRAPH 22

YIELD IN MOLS PER 100 MOLS FEED

CO
CO$_2$
USEFUL
PRODUCTS

OXYGEN TO N-BUTANE FEED RATIO
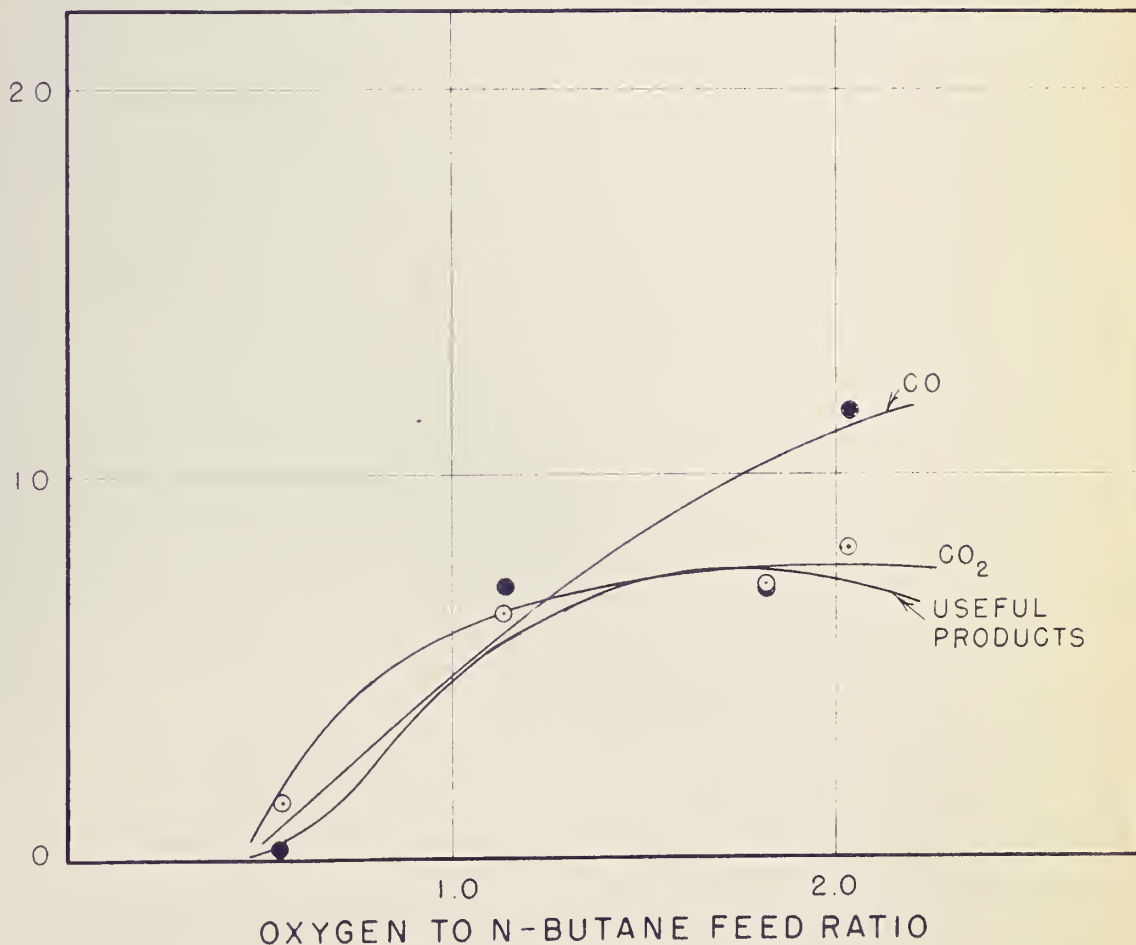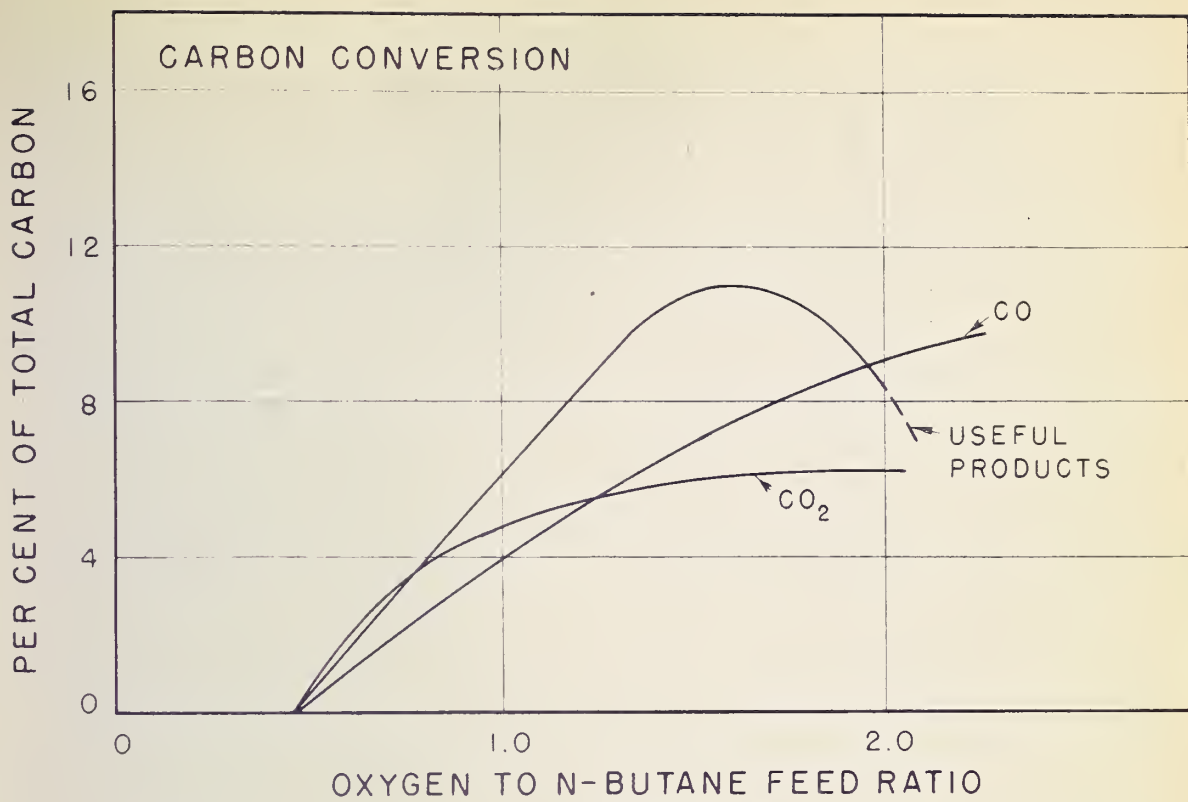
GRAPH 23

GRAPH 24

GRAPH 25

FIGURE 13

EFFECT OF VARYING OXYGEN
CONCENTRATION UPON REACTION
TEMPERATURE.
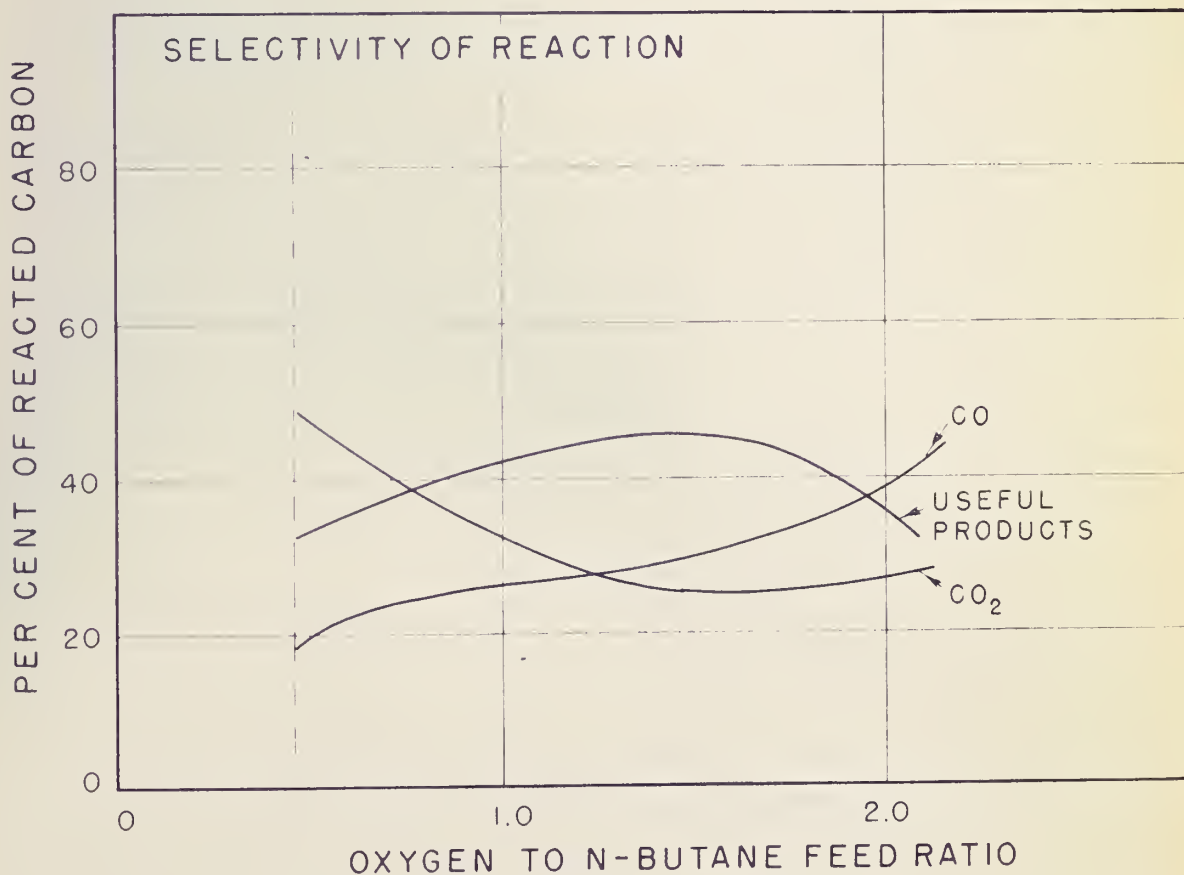
Reaction Pressure = 100 psia.
Nominal Reaction Time = 3 Sec.
Inlet Butane Concentration = 3%

This is consistent with observations from other runs. For instance, with three per cent butane and three per cent oxygen at 100 psia, the oxygen content of the offgas tends to level off at slightly higher than one percent with increased reaction time. Once the oxygen concentration is reduced below a certain point, little further oxidation can take place. The minimum value of oxygen con$_\wedge^{en}$ctration will be decreased with increased pressures as indicated earlier and will also be affected by the temperature of the reaction which is attained.

Useful product yields are believed to pass through a maximum but the results are actually indefinite. The increasing oxygen concentration increases the reactivity of the mixture and the reaction temperature, ultimately leading to complete oxidation of the hydrocarbon to CO_2, CO or water. Maximum conversion of carbon expected would be of the order of 10 per cent at an oxygen to butane ratio of approximately 1.5.
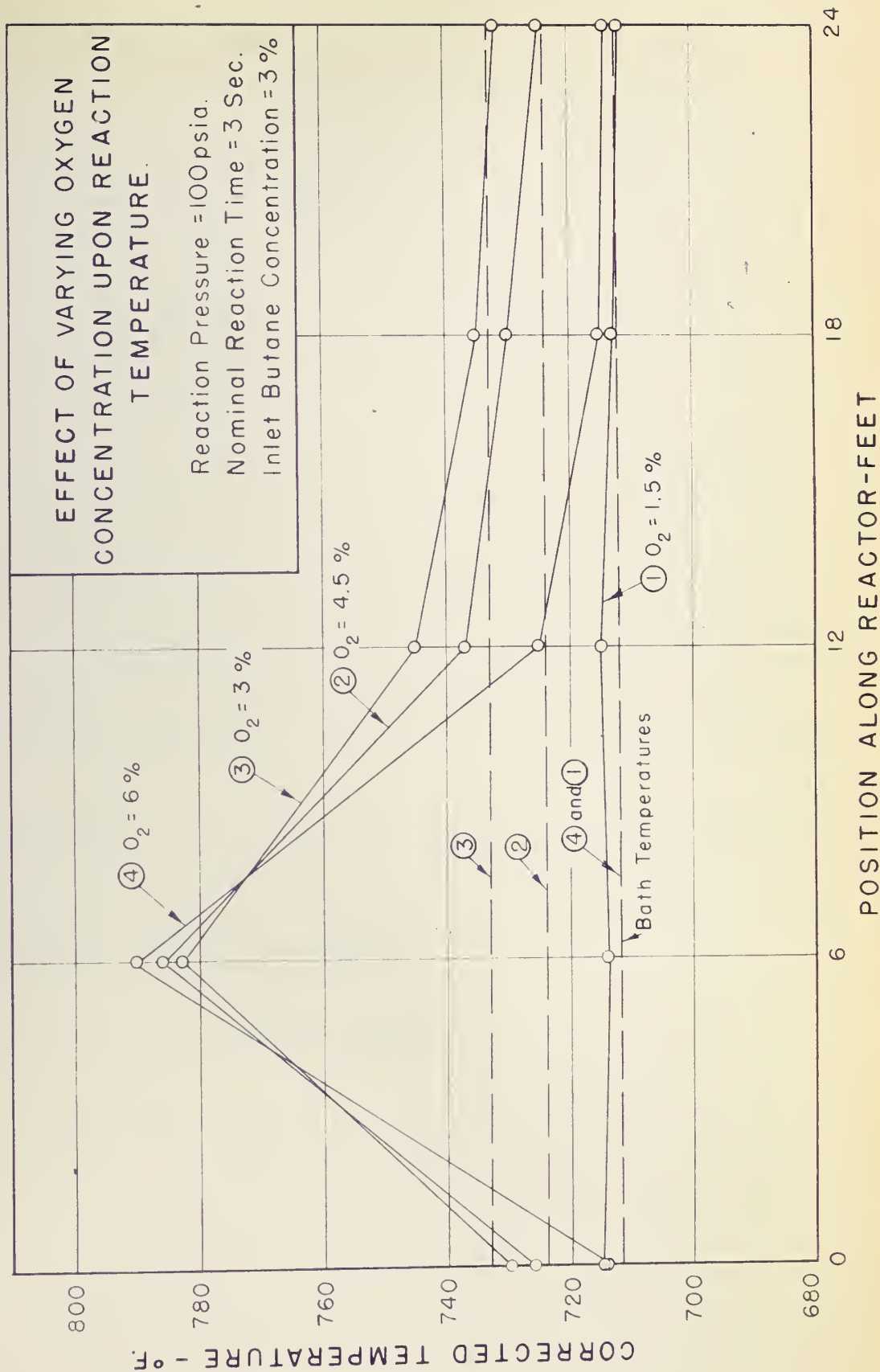
The temperature profiles indicate that a better selectivity is possible by reducing the preheat temperature because this in effect reduces the reaction temperature attained.

Thermal Effects

The experimental data which provided the thermal history of the oxidation reaction consisted of an approximate reaction temperature profile and an estimated heat of reaction. The accuracy of this information greatly affects any further treatment.

Temperature Profile

The five corrected bulk temperatures of the gas which were obtained at evenly spaced reactor intervals provide five points through which the true profile must pass. The absence of more of these temperatures obscures some of the profile characteristics which are known to occur. For a reaction time of 3.0 sec., the following features are believed to exist: an induction period before reaction initiation of the order of 0.70 sec., a curve of increasing slope after the reaction has started, the final temperature surge just before the peak, a peak of unknown extent which lies between 0.70 and 1.4 sec., a diminishing curve up to 1.8 sec. after which time, the reaction rate becomes insignificant and finally, the cooling curve which approaches the bath temperature. The following treatment is suggested to give a more clear picture of the amount of reaction occurring in various parts of the reactor.

a. To determine the proper temperature profile. Consider an elemental section, dx, of the reactor tube and from a heat balance across it

$$Q = U.P \int (t_G - t_b)\, dx$$

Q = heat transferred

U = overall heat transfer coefficient

P = perimeter of section

dx = length of elemental section

t_G = gas temperature

t_b = bath temperature

U, being nearly constant over the reactor length, may be assumed fixed in value.

The value $\int (t_G - t_b) \, dx$ corresponds to the area below the reactor
temperature curve and must equal Q/UP. The heat of reaction, Q,
may be calculated from thermal data and the product analysis. In
this way, it should be possible to fit a temperature-reactor distance
curve which will satisfy the enthalpy balance.

In practice, it may be more convenient to determine the
mean temperature driving force,

$$(t_G - t_b)_{mean} \quad = \quad \frac{Q}{UP. \; X_{Total}}$$

When this temperature is plotted on the temperature profile as a
line parallel to the abscissa, the area between the line and the
temperature profile curve must equal the area enclosed by the
temperature curve above the mean temperature.

Using this area criterion and the evidence of profile
characteristics already mentioned, a more accurate profile may be
plotted through the five known temperatures. In Figure 15, the
outline of the area shows the form of the profile which is believed
to exist.   Figure 14 shows an experimental temperature profile.

b. To find the heat liberated by the reaction in successive
sections of the reactor, the five corrected temperatures, a constant
overall heat transfer coefficient for the reactor, an accurately
determined heat of reaction and a temperature profile established from
this data are required.

Consider section 1 to 6 ft.

$$\Delta H_{1-6} \quad = \quad \Delta H_a \quad + \quad \Delta H_b$$

Figure 14.

RUN 3-A

Feb. 5/53

1. N_2-O_2 Preheat
2. Reactor Feed
3. 6 ft in Reactor
4. 12 ft in Reactor
5. 18 ft in Reactor
6. Reactor Exit
7. Butane Preheat
8. Reactor Bath

DEGREES FAHRENHEIT

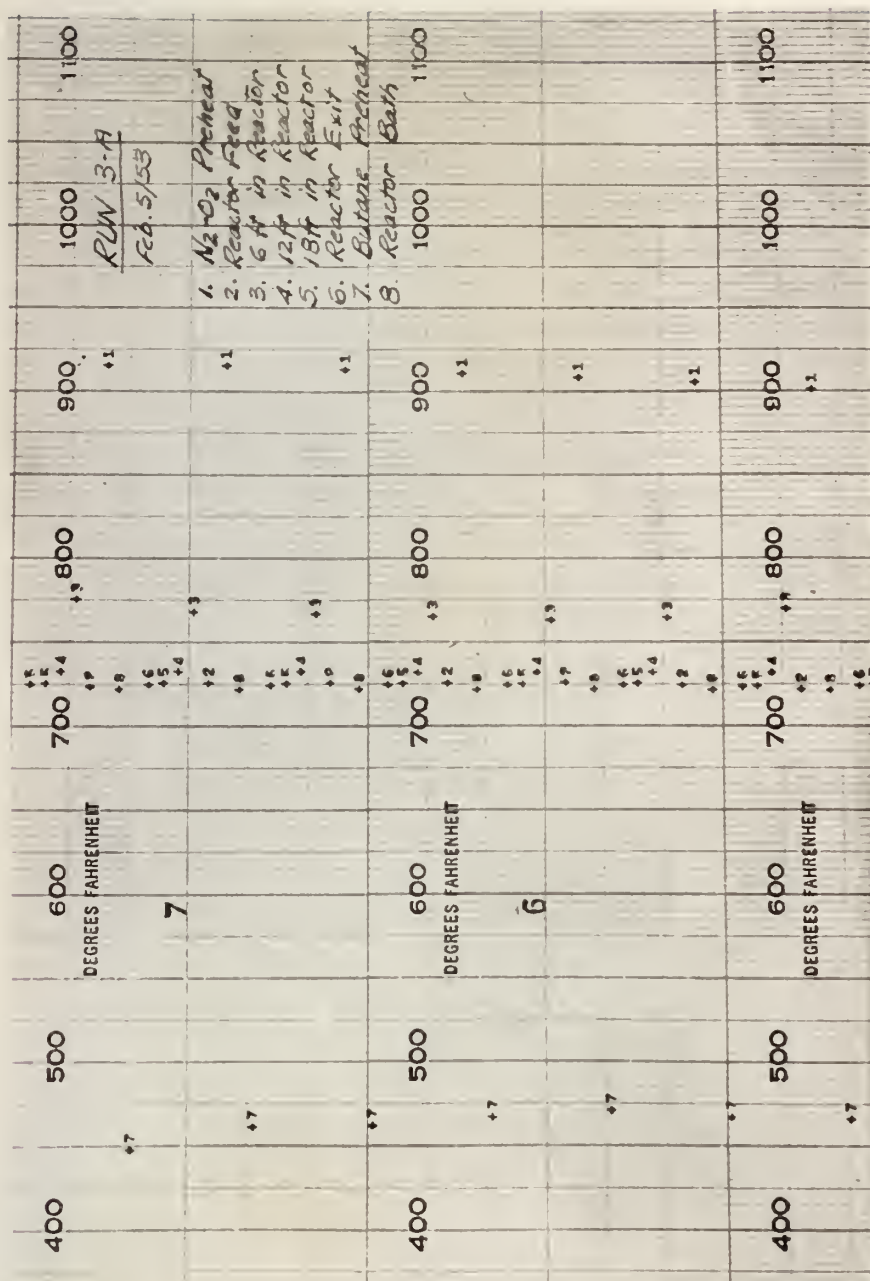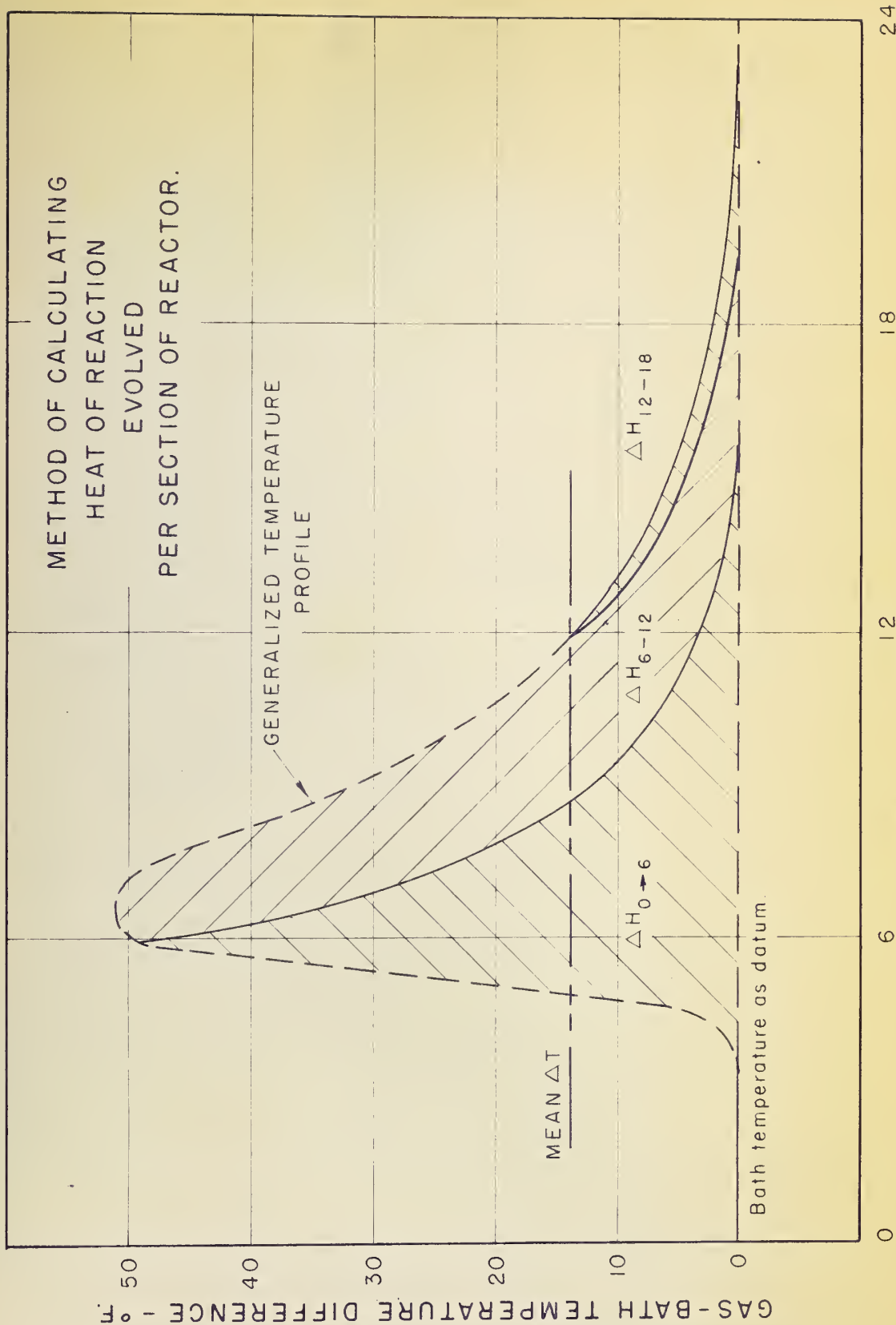METHOD OF CALCULATING HEAT OF REACTION EVOLVED PER SECTION OF REACTOR.

FIGURE 15

where ΔH_a = heat transferred to the bath

(equal to the area under the profile

from $x = 0$ to $x = 6$)

ΔH_b = sensible heat of reacting gas above

the entering temperature (obtained

by studying the temperature history

of an inert gas starting at an initial

temperature equal to that at $x = 6$ ft.

and losing its heat to the bath)

Consider each reactor section in a similar manner.

Now for section 0 to 6, ΔH_a is the area under the profile from 0 to 6 ft.

To obtain ΔH_b

Consider a differential heat balance for an inert gas being cooled

$$wCp \ dt_G = UP \ dx \ (t_G - t_b)$$

$$\frac{UP}{wCp} \int dx = \int \frac{dt_G}{t_G - t_b}$$

and $\qquad \frac{UC}{2.3 \ wCp} (x_2 - x_1) = \log \left[\frac{t_{G_1} - t_b}{t_{G_2} - t_b} \right]$

A plot of $(t_G - t_b)$ versus x on semilog paper would be linear and

of slope equal to $UP/2.3 \ wCp$. Transfer of the corresponding values

of $(t_G - t_b)$ and x to the temperature profile would appear as the

curved lines which define the ΔH/section on Figure 15.

This procedure was applied to many of the temperature profiles

and it was found that for a 3.0 sec. reaction time, $\Delta H_{12 - 18}$ was a

small percentage of the total ΔH for the reaction. In all cases,

ΔH 18-24 was insignificant. This shows graphically that no further

exothermic reaction takes place after 1.8 sec.

The application of this procedure to the experimental
data was not too satisfactory. The lack of more recorded temperatures
near the reaction peak makes any attempts to plot a complete temperature
profile rather questionable. It was also felt that some of the higher
temperatures may be as much as 10 Fahrenheit degrees lower than the
true values, even after corrections had been applied. Certainly,
several of the assumptions made in calculating the temperature corrections
are not very sound.

Reaction Characteristics

The reaction of butane with oxygen at the conditions investigated
is observed to follow a pattern which is always similar. An induction
period exists prior to the initiation of the reaction after which the
path of the reaction is largely dependent upon the heat capacity of
the gases, the ability of the reactor to cool the reaction mixture and
the reaction rate.

With the present reactor design, the reaction is carried out
under conditions neither isothermal nor adiabatic but somewhere intermediate.
If the reaction were adiabatic, a ΔH of -1 kilocal/gm-mol N_2 (considering
all feed as inert nitrogen) would cause a temperature rise of $230^{\circ}F$.
The majority of ΔH's were of the order -1.0 to -2.0 kcal/gm-mol feed.
The maximum recorded temperature rise never exceeded 90 $^{\circ}F$ compared to a
corresponding adiabatic temperature rise of perhaps 500 $^{\circ}F$. These
figures merely show that the heat capacity of the gases is not sufficient
to prevent a large temperature rise due to reaction.

The ability of the reactor to dissipate the heat of reaction is
obvious when considering the adiabatic temperature rises which were

possible and yet which did not occur. In the reactor, the heat transfer depends upon the internal area of the reactor, the temperature change from the gas to the bath and the film coefficients. Both the heat transferred and temperature difference are affected by the film resistances, which in turn have been shown to decrease with mass velocity in the reactor. The majority of runs were carried out at the same feed rate (reaction time of 3.0 sec.) so that the reactor cooling effects for these runs should be comparable. To reproduce this cooling effect in another reactor would require the same values of UA.

The reaction rate for a particular pressure and feed rate is dependent upon the concentration of the reactants and the temperature at that point within the reactor. For hydrocarbon oxidations, the surface area of the reactor also affects the rate because of its inhibitory effect upon chain propagation. The reaction rate in the butane reactor, judging from the temperature profile, increases exponentially just before the peak temperature. This temperature surge results from the inability of the thermal energy liberated to escape to the surroundings with a resulting increase in gas temperature and reaction rate. In a sense, the reaction is of the "run-away" type.

The reactions here have been shown to be neither isothermal nor adiabatic but contingent upon, the value of UA for the reactor and the kinetic rate constants for the reaction. For a small reactor, surface effects upon reaction rate may not be disregarded.

Reaction Kinetics

In determining the nature of hydrocarbon oxidation reactions, ultimately the mechanistic concepts proposed from the experimental evidence must be in accord with the kinetic data obtained for the same reaction. In the case of butane oxidation, it is doubtful whether kinetics are of value in elucidating the mechanistic concepts because of the complexity of the reaction steps and the variety of reaction products. At present, no rigorous procedure exists for the application of kinetics to this reaction. Nonetheless, the studies of such reactions are of value if the data are accurate and comprehensive so that the work is always amenable to future kinetic treatment.

Semi-empirical methods have been successfully used as a guide in scaling up laboratory reaction data but these results are specialized in application and should be considered reliable only over the restricted ranges over which they were developed. One such method is described by Reiser and Watson (25) who have applied it to a complex pyrolytic reaction. Further work on the butane oxidation project may embrace this type of study in order to make a further contribution to the development of reactor design methods. In the hope that it may be of value if such a step is contemplated, brief mention of some of the preliminary factors will now be considered. It will be necessary to fix the feed composition, initial temperature and pressure of the reaction and to obtain data relating space velocity to the conversion. An analysis of optimum conditions, based on this study, is included in the conclusions following this section. The design of a new reactor should include

means of determining the effect of reactor surface to volume ratio.
Mass flows of higher turbulence than encountered in this investigation
should be planned in order to ensure complete mixing and eliminate
radial thermal gradients. The application of the principles outlined
by Reiser and Watson is facilitated if an exact temperature profile
of the reaction is available. The $\Delta H/$ section approach would be of value
here if the sections are small enough and the ΔH values accurate because
the conversion per section based on the average temperature of the
section may be checked against the known value of ΔH.

The above treatment is hardly satisfactory but since no appli-
cation of the method to this project has been attempted as yet, it can
only be hoped that the above information is of some value.

CONCLUSIONS AND RECOMMENDATIONS

The complexity of hydrocarbon oxidation studies has been indicated by this work. Little is known regarding the mechanism and kinetics applying to these reactions. Further work on the butane project should be more restricted in scope and certainly more exact so that the quantitative results may be valid without question. The application of semi-empirical rate analysis treatment is recommended at this stage because of its value to the design of reactors for complex reactions. With more extensive knowledge of the thermal history of the reaction, the semi-empirical approaches may become more rigorous.

The study of butane oxidation indicated that the major products included methanol, ethanol, acetaldehyde, acetone and formic acid. The reaction exhibited the characteristics of a chain reaction because of the existence of an induction period of approximately 0.70 sec. A critical oxygen concentration of the order of 1.5 per cent was observed for the reaction at 100 psia and 725°F, in the particular reactor. With butane concentrations equal or greater than the critical oxygen content, no reaction was initiated and the conjecture is raised that the oxygen concentration is critical to the propagation of the chain reaction. Substantiation of this point may lie in further testwork at the same reaction conditions but with different reactor surface to volume ratios.

The reaction temperature history follows a characteristic profile, the appearance of which has only been estimated and is subject to the

thermal characteristics of the reactor. The reaction occurred under conditions which were neither adiabatic nor isothermal but somewhere intermediat

The peak yields of those intermediate products of economic value were obtained in reaction times of the order of 1.0 to 1.5 seconds. The effect of nitrogen in suppressing the reaction is believed to result primarily from reactant dilution. Increasing pressure greatly affected reaction rates even to the point where complete oxygen reaction was attained. Excess butane (greater than a one to one butane-oxygen ratio) was observed to decrease yields of useful products. Varying the feed composition altered the course of the reaction very significantly. Table 6 summarizes some of the test results:

Table 6

Parameter	Pressure	Reaction Time	N_2 Diluent	Butane	Oxygen
Pressure (psia)	variable	100	100	100	100
Reaction time (sec.)	3.0	variable	3.0	3.0	3.0
% C_4H_{10}	3.0	3.0	1:1 ratio	variable	3.0
% O_2	3.0	3.0		3.0	variable
Range tested	50-175	0.8-4.5	88-97% N_2	1.5-6.0	1.5-6.0
Limiting value	50	1.0	97	None	1.5
Optimum range	115-135	1.0-2.0	95.5-96.5	3.0-4.5	3.5-5.0
Optimum Conversion (%)	13	9	22	10	10

Further similar butane oxidation experimentation should be
restricted to the following conditions: for a reaction initiation temperature
of 725°F, an oxygen-butane ratio of one to 1.25 with reaction time of the
order 1.0 to 1.5 sec.; for four per cent oxygen, a pressure of 100 psia;
for three per cent oxygen, a pressure of 125 psia. Decreasing oxygen
below three per cent may improve the selectivity of the reaction but the
more dilute gas will intensify analytical and product recovery problems.
Oxygen above four per cent may not be too satisfactory because the increased
reaction rate could only be offset by reducing the pressure below 100 psia
with consequent loss of efficiency in conversion. The above suggestions
apply to single-pass reactions because no testwork involving recycle was
attempted.

Design of a new reactor should include provision for accurate
measurement of the temperature history. The heat transfer from the
reactor and turbulence in the gas stream should also be considered.

The use of an aroclor reactor bath is not satisfactory for a larger
scale reactor but may be justified in laboratory use requiring boiling
at temperatures up to 730°F over a cumulative period of two weeks. With
the small reactor, the change in aroclor properties, the rapid tube
fouling and maintenance difficulties still present problems. The over-
all heat transfer coefficient may decrease with time and no independent
control of the bath coefficient is possible without forced circulation.

The preheaters were satisfactory but their temperature control
requires much improvement to eliminate manual supervision.

The product absorption tower is not entirely satisfactory. Loss of aldehyde vapour occurred in all runs but those with slight reaction and the best absorption was obtained with the tower partially flooded. Some work may be required to determine appropriate absorption coefficients for the tower so that the proper water feed rate can be calculated.

The nitrogen-oxygen storage pressure reduction valve must be replaced with a more reliable valve or else the offgases should be passed through a rotameter in order to obtain constant conditions of measurement.

The mass spectrometer analyses should be checked, now that the main constituents are known, with some of the chemical analytical methods indicated in the appendix. Product solutions may be concentrated by distillation and the residual solution checked chemically for organic content. If this concentration was nearly complete, very reliable mass spectrometer analyses could be available, even to the detection of other trace constituents.

Ultimate carbon analyses of these concentrated solutions should be re-attempted. Failing this, it may be feasible to use a 50 cc. (approximate figure) sample and evaporate it in a sealed system, dilute the vapours with nitrogen and use the copper oxide furnace as a means of estimating the carbon content.

Titrations with mixed indicator should be carefully checked with measured weights of C.P. Na_2CO_3 to establish the true endpoints. This precaution is mentioned because faulty analytical technique will cause a large error.

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APPENDIX

Nomenclature

Q - steady state rate of heat transfer, BTU/hr.

U - overall heat transfer coefficient, BTU/(hr.)(sq.ft.)($^\circ$F)

h - convective heat transfer coefficients for films,   "

h_r - simplified radiation heat transfer coefficient,   "

ϵ - emissivity, dimensionless

A - area of heat transfer surface, sq.ft.

P - perimeter of section, ft.

X - length of section, ft.

ΔT_{LM} - log mean temperature difference (F°)

t - temperature (subscripts G for gas, b for bath,

      W for wall, c for indicated temperature), $^\circ$F

D - diameter of circular cross-section, ft.

De - modified diameter for use with annuli, ft.

D_H - diameter of helix, ft.

G - mass velocity, lb/(hr.)(sq.ft.of cross section)

μ - absolute viscosity, lb/(hr.)(ft.)

Cp - specific heat at constant pressure, BTU/(lb.)($^\circ$F)

k - thermal conductivity, BTU/(hr.)(ft.)($^\circ$F)

W - mass rate, lb/hr.

Representative Treatment of Experimental Data.

Run No 7-A

Length of run   - 41.76 min.

Pressure   - 100 psia.

Bath temperature = 726.5 °F

Average inlet temperature - 727°F

Offgas analysis by Orsat (per cent dry)

CO - 0.90 CO - 1.22 O_2 - 1.15 Unsaturate - 0.70

Total volume offgas - 51.7 cu.ft. at 75°F and 27.4 in. Hg

Vapour pressure of water - 0.90 in. Hg at 75°F

Liters/cu.ft. - 28.3

Liters/gm-mol - 22.4

Calculations:

Gm-mols offgas (dry) = 51.7 $\frac{(28.3)(27.4 - 0.9)(492)}{(22.4) \quad 29.9 \quad) 535)}$ = 53.2

Nominal reaction time (based on offgas)

Transverse reactor area = 0.104 sq. in.

Reactor length   = 24 ft.

Velocity of gases at 100 psia and 727 F

= $\frac{1}{60} \frac{(51.7)}{(41.76)} \frac{13}{100} \frac{(1187)}{(535)} \frac{144}{0.104}$ = 8.24 ft/sec.

Reaction time = $\frac{24}{8.24}$ = 2.91 sec.

Offgas sampler

Vol. measured = 0.0710 cu.ft. at 84°F and 23.7 in. Hg

Gm-mols (dry) $= 0.0710 \frac{(28.3)}{(22.4)} \frac{492}{544} \frac{(23.7-1.2)}{(29.9)} = 0.0611$

CO_2 removed $= \frac{6.0}{1000} (0.0898 \text{ N}) = 0.000539$ gm-mol

Aldehyde removed $=$ nil

therefore % CO_2 in offgas $= \frac{0.000539(100)}{0.0611 + 0.0005} = \underline{0.87}$

(checks with Orsat analysis)

Total gm-mol sampled $= 0.0616$

Ratio of offgas to sample $= \frac{53.2}{0.0616} (0.985) = \underline{850}$

(where 0.985 is correction factor for low meter reading)

Carbon balance: basis of 41.76 min. operation

Carbon in — 247 cc. $C_4 H_{10}$ at 80°F

$= 247 \frac{(0.590)}{(58.08)} 4 = \underline{10.0}$ gm-atom carbon

Carbon out

as CO_2 in offgas $= \frac{0.90}{100} (53.2) = 0.479$

as CO in offgas $= \frac{1.43}{100} (53.2) = 0.760$

as unreacted hydrocarbons in offgas

$= 850 \frac{(115.8)}{(1000)} 0.0898 \text{ N } - \text{ CO}$

$= 8.84 - 0.76$ $= 8.08$

as absorbed products

$= \frac{(1.146 \text{ % C})(1755\text{ml})(\text{sp gr } 1.0)}{100\%} = 2.01$

as unabsorbed products $=$ nil _____

therefore gm-atom carbon out $=$ 11.33

Ratio of carbon out to carbon in $=$ 1.13

Adjusted carbon balance

The high value of carbon out may be attributed to the unreacted hydrocarbon titration and the carbon balance will be adjusted on this basis:

Unreacted hydrocarbons $=$ 10.0 - 0.48 - 0.76 - 2.01

$$= \underline{6.75} \text{ gm-atom carbon}$$

gm-mol unsaturates in offgas $= \dfrac{0.70(53.2)}{100} = 0.37$

Assume unsaturates are C_2H_4

gm-atom carbon in unsaturates $= 2(0.37) = 0.74$

Assume saturated hydrocarbons are C_4H_{10}

gm-atom carbon in saturated $h_c = 6.75 = 0.74 = 6.01$

and gm-mol $C_4H_{10} = \dfrac{6.01}{4} = \underline{1.50}$

Nitrogen balance : basis of 41.76 min.operation

Total impurities in offgas (by Orsat) $=$ 3.97%

Nitrogen in $=$ nitrogen out $= 53.2 \dfrac{(100-3.97)}{100} - 1.50$

$$= 51.0 - 1.50 = 49.5 \text{ gm-mol}$$

Inlet gas composition

$N_2 - O_2$ feed contained 4.90% O_2

N_2 in feed $= 49.5$ gm-mol $= 90.75\%$

O_2 in feed $= \dfrac{4.90(49.5)}{95.10} = 2.55$ " $= 4.67\%$

$$C_4H_{10} \text{ in feed} = \frac{10.0}{4} = 250 \text{ gm.mol} = 4.58\%$$

$$54.55 \quad "$$

Space velocity $= \dfrac{(cu.ft.at\ NTP)}{(hr.} \dfrac{(\quad 1 \quad)}{)(cu.ft.of\ reactor)}$

$$= \frac{54.5}{41.76} \frac{(22.4)}{(28.3)} \frac{144}{24} \frac{(60)}{(0.104)} = 3580 \text{ l/hr.}$$

Feed rate $= 54.5 \dfrac{(60)}{(41.76)} = 78.4 \text{ gm.mol /hr.}$

Knowing the feed rate and the total gm-mol of useful products

in the aqueous solutions, the following converted figures may

be obtained

Methanol $=$ 1.26 gm-mol/100 gm-mol feed

Ethanol $=$ 0.195 "

Acetaldehyde $=$ 0.533 "

Acetone $=$ 0.124 "

Formic acid $=$ nil "

Total 2.11

Oxygen balance : basis of 100 gm-mol feed

Oxygen in

gm-mol oxygen $=$ 4.67

Oxygen out

as unreacted O_2 $= \dfrac{1.15\ (53.2)}{100} \dfrac{100}{54.5} = 1.12$

as CO_2 $= 0.479 \dfrac{(100)}{(54.5)} = 0.879$

as CO $= \dfrac{0.760}{2} \dfrac{(100)}{(54.5)} = 0.697$

as methanol $=$ $\dfrac{1.26}{2}$ $= 0.63$

as ethanol $=$ $\dfrac{0.195}{2}$ $= 0.097$

as acetaldehyde $=$ $\dfrac{0.533}{2}$ $= 0.266$

as acetone $=$ $\dfrac{0.124}{2}$ $= 0.062$

gm-mol oxygen out $\qquad$ 3.75

therefore gm-mol water (by difference) $=$ 1.84

Hydrogen balance: basis of 100 gm-mol feed

Hydrogen in

gm-mol hydrogen $= 2.50\ (5)\ \dfrac{100}{54.5}$ $=$ 22.9

Hydrogen out

as unsaturated h.c. $= 0.37\ (2)\ \dfrac{100}{54.5}$ $= 1.36$

as saturated h.c. $= 1.50\ (5)\ \dfrac{100}{54.5}$ $= 13.8$

as methanol $= 1.26\ (2)$ $= 2.52$

as ethanol $= 0.195\ (3)$ $= 0.585$

as acetaldehyde $= 0.533\ (2)$ $= 1.07$

as acetone $= 0.124\ (3)$ $= 0.372$

as water $= 1.84$

gm-mol hydrogen out $\qquad$ 21.5

Yields: basis of 100 gm-mol feed

CO_2 $= 0.88$ gm-mol

CO   = 0.70   gm-mol

Useful Products = 2.11 "

Thermal data

Heat of Reaction

The heat evolved during the reaction may be
calculated from heat of formation and heat capacity
data obtained in the literature and applied to the
experimental data. An enthalpy balance across the
reactor and based on 100 gm-mol feed indicated the
total heat liberated.

Referring to an enthalpy of zero for the
elemental state at $25^{\circ}C$ ($77^{\circ}F$) and 1 atm, C = solid,
O_2 = gas, H_2 = gas, N_2 = gas and neglecting the
change in enthalpy resulting from an increase in pressure,
the following net molar enthalpies were used:

Compound	ΔH Formation	Sensible heat	Net enthalpy	Reference
	kcal/gm-mol at 770°F, 1 atm.	at 725°F kcal/gm-mol	kcal/gm-mol	
N_2	0	2.46	2.46	(1) $Cp = 6.5 + 0.001\,T$
O_2	0	2.66	2.66	(1) $Cp = 8.27 + 0.000258\,T - 187700/T^2$
* C_4H_{10}	-29.81	11.35	-18.46	(2)
+ C_2H_4	12.50	5.85	18.35	(2)
H_2O	-57.80	4.69	-53.11	steam tables
CO_2	-94.05	3.74	-90.31	(1) $Cp = 10.34 + 0.00279\,T - 195500/T^2$
CO	-26.42	2.53	-23.89	(1) $Cp = 6.60 + 0.0012\,T$
CH_3OH	-48.08	** 5.77	-42.31	(3) $Cp = 0.50$ cal/gm extrapolated
C_2H_5OH	-52.23	** 8.29	-43.94	(3) $Cp = 0.50$ cal/gm extrapolated.
CH_3CHO	-39.72	** 7.13	-32.59	(3) $Cp = 0.45$ cal/gm extrapolated
CH_3COCH_3	-51.79	** 9.50	-42.29	(3) $Cp = 0.45$ cal/gm. extrapolated
$HCOOH$	-86.67	++ 9.52	-77.15	$Cp = 0.45$ cal/gm estimated

*   Unreacted saturated hydrocarbons assumed n-C_4H_{10}

**   Heat capacity data at elevated temperatures not

available and so, data used may be unreliable

\+   Unreacted unsaturated hydrocarbons assumed C_2H_4

\+\+   No heat capacity data for gaseous formic acid

available.

References:

1   Perry, "Chemical Engineers' Handbook",

    Mc Graw-Hill, 1950

2   Kirkbride, "Chemical Engineering Fundamentals",

    McGraw-Hill,   1947

3   "Handbook of Chemistry and Physics", Chemical

    Rubber Publishing Co., 27th Edition.

Enthalpy balance over reactor :   basis of 100 gm-mol feed

Feed gas	gm-mol	ΔH	Off gas	gm-mol	ΔH
N_2	90.75	223	N_2	90.75	223
O_2	4.67	12.4	O_2	1.12	2.99
C_4H_{10}	4.58	-84.4	C_4H_{10}	2.76	-50.9
			C_2H_4	0.68	12.5
			H_2O	1.84	-97.8
			CO_2	0.879	-79.4
			CO	1.39	-33.4
			CH_3OH	1.26	-53.3
			C_2H_5OH	0.195	-8.6
			CH_3CHO	0.533	-17.4
			CH_3COCH_3	0.124	-5.2
			$HCOOH$	-	-
	235.4	-84.4		238.5	-346.0

$$\Delta H_1 = +151.0 \qquad \Delta H_2 = -107.5$$

therefore, ΔH of reaction

$$= \Delta H_2 - \Delta H_1$$

$$= -107.5 - 151.0 = -258.5 \text{ kcal/100 gm-mol}$$

of feed

Reaction Temperature

For Run No. 7-A, the following average temperatures were recorded:

	°F	Max. Variation	Mean Deviation
Reactor entrance	727	722-731	1
6 ft. in reactor	788	770-796	5
12 ft. in reactor	741.5	732-744	3
18 ft. in reactor	728	726-730	0.4
Reactor exit	728	727-730	0.3
Bath	726.5	726-727	0.5

Because of the small section of the thermocouple well which was exposed to the gases within the reactor tube, an attempt was made to correct the recorded temperature for errors caused by the heat losses from the well through conduction and radiation. The following equation was developed for this purpose and its derivation is also included in the Appendix:

$$\Delta t = (tc - tw) \left[\frac{\left(\frac{h_r \epsilon}{h_c} \text{Cosh } ml + 1\right)}{(\text{Cosh } ml - 1)} \right]$$

Application of the equation involved the following steps:

1. The corrected temperature, t_G , was estimated

2. Using the reactor gas and bath film coefficients and bath and gas temperatures, t_W was estimated.

3. The value of h_c was calculated from $h_c = 5.95 \ W^{0.6}$

4. The value of h was obtained from a graph in McAdams, "Heat transmission".

5. From these values, the equation was solved.

6. If the calculated t_G did not correspond with the estimated value, the procedure was repeated using the new value for t_G

For Run No. 7-A, the following corrected temperature profile was obtained:

Entrance	6 ft.	12 ft.	18 ft.	Exit
727	805	746	728	728

Analytical Methods

Determination of unabsorbed aldehydes

Dodge[1] and co-workers mention use of 2,4-dinitrophenylhydrazine as a means of quantitative determination of aldehyde and ketone vapours. This procedure involved precipitation of the carbonyl molecule by contact with a solution of the phenylhydrazine. The solution used in the fritted glass bubbler was prepared by acidifying a nearly saturated 2, 4 - dinitrophenylhydrazine solution until 2 N with hydrochloric acid. The acid was added to eliminate possible CO_2 absorption.

In using this method, the fritted glass bubbler was found to plug with the precipitate and so, another preliminary bubbler, containing distilled water, was used to dissolve the major part of the aldehyde vapour. The precipitate was largely formed when the two bubbler solutions were combined upon completion of the reaction run.

The precipitate was measured gravimetrically but for accurate work, neither the method nor phenylhydrazine are recommended because of the slight solubility of the aldehyde

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1 Bretton, Wan and Dodge, Ind. Eng. Chem., 44, 594 (1952)

phenylhydrazones in water. Acetone vapours would introduce
even larger error because of the greater solubility of this
precipitate. These last factors were noted when tests were
performed on blank solutions.

In interpreting the results, all of the precipitate
was assumed to be acetaldehyde This assumption is not
unreasonable when considering the large difference in volatility
between acetaldehyde and the balance of the useful products.
Preparation of CuO catalyst

Commercial grade copper oxide catalyst pellets were
tested and found to be inefficient for oxidation of
hydrocarbons at elevated temperatures. A more sensitive catalyst
containing one per cent iron oxide was prepared in the
following manner:

Enough Cu $(NO_3)_2$ and Fe $(NO_3)_3$ were dissolved in
three liters of distilled water to give 100 gm. of 99:1
CuO - Fe_2O_3 after which 30 per cent KOH was added until slightly
in excess. The mixture was boiled for 20 minutes, cooled and
the precipitate washed by successive decantations. The mixture
was then filtered, and while moist, the precipitate was
pressed into small pellets. These pellets were dried, reduced with
H_2 at 400°C and re-oxidized with air at 400°C. Too rapid oxidation
will cause development of high temperatures resulting in sintering
of the catalyst.

When used at 700 C, this catalyst was **far** superior to the commercial CuO catalyst, oxidizing quantitatively all hydrocarbons and carbon monoxide.

Preparation and use of mixed indicator

In titrating the KOH bubbler solutions, use of
phenolphthalein and methyl orange indicators in successive
titrations gave unreliable results. The phenolphthalein
end-point was never clearly indicated but "faded" in the
course of the titration.

To avoid this, a mixed indicator which gave an
end-point over a smaller pH range, 8.2 - 8.4, was used. The
stoichiometric point where one mole of hydrogen ion has been
added per mole of carbonate ion occurs at pH = 8.4. The
colour change of the mixed indicator extends from violet to
yellow, the latter colour indicating a pH of 8.4. The
resulting yellow colour is of the same intensity as that of
alkaline methyl orange and does not obscure the methyl orange
endpoint which is orange.

The methyl orange endpoint was taken at the first
appearance of an orange tinge. The titration between the two
end-points was taken as directly equivalent to CO_2 on a mole
basis. To reduce errors, the N/10 HCl was standardized with dry
C.P. Na_2CO_3 using methyl orange and mixed indicators. Blanks
were always run on the 3N KOH solutions used for CO_2 absorption.

The blank value was deducted from the measured HCl required to titrate
the sample.

The mixed indicator was prepared as follows:

1 pt. 0.1% Cresol red sodium salt in H_2O

3 pt. 0.1% Thymol blue sodium salt in H_2O

Ultimate carbon analysis

The standard ultimate carbon procedure was modified
for application to volatile organic liquids. The standard
apparatus consists of a horizontal tube which is placed within
a furnace. A measured amount of sample, when placed within the
tube, is oxidized with an oxygen stream, CO_2-free and dry, at
the necessary furnace temperature. The stream of gases then
pass over a series of metallic oxide catalysts to complete the
conversion of carbon to CO_2. The water and CO_2 were removed
after leaving the tube with a $MgCl_2$ drying tube and
concentrated KOH and Ascarite absorber. The CO_2 which was
absorbed was determined gravimetrically.

To oxidize organic liquids, a sample of the liquid
was weighed in a small high-temperature glass tube filled
with an inert porous material such as kieselguhr, held in
place with asbestos pads. Rubber caps were fitted over the
ends of the tube and they were only removed prior to
inserting the sample tube in the furnace.

Literature Review of Analytical Methods.

Useful oxygenated organic products from the partial butane oxidation process were recovered as aqueous solutions. However, efficient operation of the absorption tower with a lean feed gas required large water to product ratios. With product samples obtained in preliminary runs, Duthie attempted to find the nature and quantity of the solution constituents. Chemical analysis involved Romijn's cyanide method for formaldehyde (25) and direct titration, with standard caustic, of total acids. Separation of the compounds was attempted by fractionation in a Podbielniak Hypercal Unit. Physical measurements such as refactive index were taken of these distillation cuts but the estimated analyses which he presented were rather questionable.

A literature search was now made for quantitative specific and group chemical methods which were applicable to analysis of the product solutions and distillation fractions. Later distillation attempts showed that the products constituted too low a percentage of the total volume of liquid to obtain sharp quantitative separations.

Failure of the distillation separation and absence of any preliminary identification work on the products resulted in turning to the mass spectrometer as a means of identification and quantitative determination. Accordingly, representative product

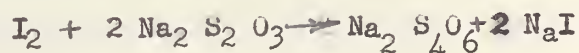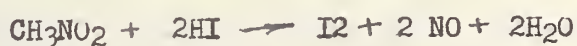samples were sent to the Analytical Service Department of
the Consolidated Engineering Corporation, Pasadena,
California, for mass spectrometer analysis.

The earlier work which involved a literature
survey for chemical analytical methods and some testwork
on the selected methods was not used advantageously.
However a summary of this survey is included in this report
in the hope that it may be of future value.

The literature search was focused upon specific and group methods of analyzing aqueous mixtures of organic alcohols, acids, ketones and aldehydes.

Alcohols

The chemical determination of alcohols in aqueous solutions appears very difficult because the presence of water eliminates, in most cases, approaches involving substitution reactions with the alcohol hydroxyl radical. Only one procedure was noted which seemed generally applicable. Fischer and Porter (8) devised a quantitative procedure applicable to methanol and ethanol, and which with some modification would be applicable to propanol. The reactions involved are as follows:

$$CH_3OH + HNO_2 \longrightarrow CH_3NO_2\uparrow + H_2O$$

$$CH_3NO_2 + 2HI \longrightarrow I_2 + 2NO + 2H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The alcohol is liberated from the solution as a volatile nitrite which oxidizes HI to free iodine which in turn may be titrated directly with standardized $Na_2S_2O_3$. Methanol and ethanol form nitrites volatile at room temperature and the actual separation occurs when these nitrites are liberated. Application to propanol (b.p. $C_3H_7NO_2 = 57^oC$) appears feasible unless its reaction rate is too retarded. Chalov and Volskaya (6) have modified this method to speed up the procedure and

minimize the equipment required but the accuracy of the
method may be reduced.

If the alcohol is solid or nearly pure,
esterification techniques (19) involving use of acetyl
chloride, acetic onhydride or phthalic anhydride in inert
solvents are applicable, e.g.

$$
\text{acetyl chloride and pyridine}
$$
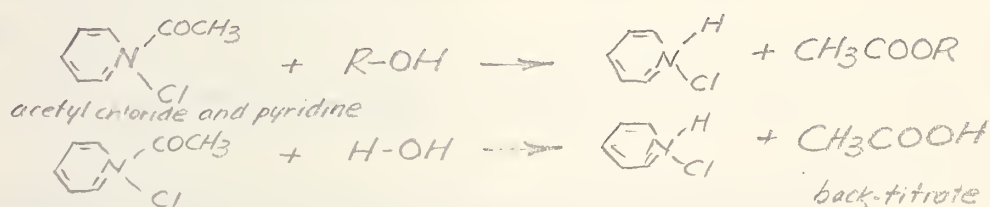
This example procedure (22) carried out in an inert solvent
such as toluene may be used if very little water is present
and it minimizes the unfavourable effects of low molecular
weight aldehydes. Error is introduced by some esters and
easily hydrolyzed compounds which release acidic or basic
constituents. However, acids could be determined separately
or corrections applied for some types of interfering compounds.

Many workers (1,21,5) discuss oxidation methods
where the alcohol is oxidized to an aldehyde, acid, or
completely to a carbonate but little mention is made of
quantitative results. In these procedures, strong

$$R-CH_2OH \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH \xrightarrow{[O]} CO_2$$
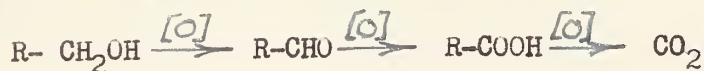
oxidizing agents are required and their application to a
mixture of alcohols appears unreasonable because of the variety

of products formed and the varying degrees of oxidation
which are possible. If the aldehydes were not separated from the
alcohols initially, their oxidation would also obscure the
results. However, should an oxidation technique be found
applicable, Stamm (24) discusses a newer controlled
oxidation reaction using permanganate in slightly alkaline
media, e.g.

$$MnO_4^- \longrightarrow MnO_4^= \quad - 1e$$
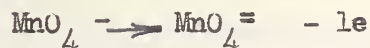
No mention is made of specific results from oxidation of
organic molecules.

Another recent approach (13), discussed but not
directly applied, involves use of Karl Fischer reagent in
determining the hydroxyl radical. This procedure appears
feasible only with very low water content in samples or when
water content may be measured separately.
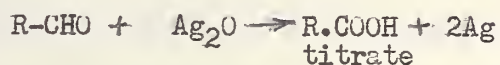
Aldehydes and ketones

The majority of reactions with this family of
compounds involve the more active carbonyl group linked to
an alkyl radical and hydrogen atom or to two alkyl
radicals. Many well known aldehyde reactions such as action
with Fehling's Solution, Tollen's Reagent, or Schiff's
Reagent may be used as qualitative tests but do not appear
directly applicable quantitatively because of possible
interferences in complex mixtures of organic compounds.
Easily oxidized compounds react with Fehling's and Tollen's
tests. Acetone will also react but more slowly with Schiff's
Reagent. The haloform reaction is applicable only to
compounds having a methyl carbonyl group such as acetaldehyde
and acetone. In any case when an unknown mixture of products
is involved, results of these tests could be misleading.

Methods which appear directly applicable involve
addition reactions with the carbonyl group with or without
expulsion of water. Siggia and Maxcy (20) have modified the
wellknown bisulfite reaction so that it is volumetric,
quantitative and specific for aldehydes providing ketones
present are less than 10 mol per cent.

$$R-CHO + Na_2SO_3 + H_2O \rightleftharpoons R-C\begin{smallmatrix}H\\OH\end{smallmatrix} + NaOH$$
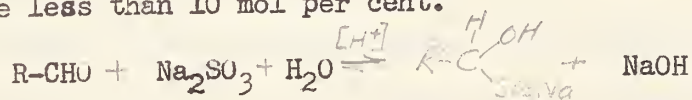
Acetals do not interfere. This method was tested with

formaldehyde and acetone solutions and found to be quite

satisfactory. Mitchell and Smith (14) have modified the

application of Tollen's Reagent for the determination of

aldehydes in the presence of ketones. Their method

$$R\text{-}CHO + Ag_2O \longrightarrow R.COOH + 2Ag$$
$$\text{titrate}$$

gives low results for formaldeyde and acetaldehyde

determinations require a special technique because of its

volatility. The reaction of both aldehyde and ketones with

hydroxylamine has been studied and volumetric techniques

developed. Bryant and Smith (4) have reported a procedure

requiring titration of the HCl released in the reaction which

is carried out in a pyridine environment. Steric hindrance

however prevents reaction with methyl carbonyl groups and strong

acids will interfere with the titration. In a later

application, Smith and Mitchell (23) alter the method so that

it is generally applicable and acetals may also be determined

separately. The reaction is carried

$$NH_2OH. HCI + RCHO \longrightarrow RC(H) = NOH + H_2O + HCI$$

$$NH_2OH. HCI + RCOR' \longrightarrow RR'C = NOH + H_2O + HCI$$

out in alcohol and the presence of up to 10 ml. of water may

be corrected with a blank determination. This latter procedure

was also tested and found to be satisfactory for butane product

analysis.

Reynolds and Irwin (17) have published a review
of analytical methods for determining formaldehyde and other
aldehydes and some of their references which were consulted
are included in this article. Quantitative separation of
aldehydes by crystallization as copper salts of hydroxamic
acid in the Angeli-Rimini reaction (18) was mentioned.

The reactions discussed so far involve group
determinations. However some claims are made for specific
reactions. Walker (25) has improved Romijn's cyanide method
for specific determination of formaldehyde. Acetone greater
than 50 mol per cent and acetaldehyde above five mol per cent
are said (17) to interfere. A more recent method (3), based on
a colorimetric determination with chromotropic acid, is simpler
and the only interference, that of acetaldehyde, may be
eliminated by increasing the ratio of reagent to formaldehyde.
Use of O-nitro benzaldehyde or salicyl aldehyde for specific
colorimetric determination of acetone is claimed (12) but
another reference (11) indicates this reaction is specific for
any methyl ketone and that acetaldehyde will also react. A
specific colorimetric test for acetaldehyde is mentioned.
(17, 7, 9) but the only procedure located (17) states "...
to aldehyde solution add saturated solution of piperazine hydrate
and four per cent solution of sodium nitroprusside. The
intensity of blue colour developed is measured on an absorptiometer
with light of wavelength, 5700A°." This method appears similiar

to Legal's or Rothera's tests (10a) for acetone using
sodium nitroprusside in alkaline media.

Oxidation techniques mentioned earlier (16,24) may
be applicable but they are subject to the same criticisms when
applied to complex solutions.

Other methods for aldehyde determination use a
polarograph or chromatographic absorption. The former technique
is claimed satisfactory (2,26) for formaldehyde and
acetaldehyde but the presence of other compounds with close half-
wave potentials may alter its utility. No immediately
applicable chromatographic method was located in the literature.

Acetals may also be estimated in Smith and Mitchell's
oxime procedure (23) for aldehydes and ketones.

Acids

Neutralization of the acids with standard alkali solutions represents the simplest means of quantitative determination. The presence of aldehydes may interfere with a direct titration of the aqueous solution by obscuring the true endpoint. However, Mitchell and Smith (23) also state that aldehyde interference may be eliminated by titration with alcoholic KOH in an alcoholic medium. The pH should be obtained potentiometrically when the true endpoint is unknown.

Esters may be saponified with standard alkali and back-titrated under similiar conditions.

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Heat Transfer from the Reactor.

The butane oxidation reactor, a helical coil, was immersed in a bath of boiling Aroclor and the heat evolved from the reaction within the coil was transferred from the gases to the bath which was at a constant lower temperature. Some knowledge of the gas and bath film heat transfer coefficients was required to interpret the nature of the reaction properly. Durno and Hantho[1] calculated heat transfer coefficients from experimental data obtained by heating and cooling air in the butane reactor. Later work indicated that their values for the coefficients might be inaccurate because the temperatures used were subject to error. The thermocouple wells used for the thermocouples were influenced by heat losses through the well wall and also by radiation to or from the reactor wall. Accordingly, an attempt was made to correct the temperatures and the heat transfer coefficients were recalculated on this basis.

Their experimental work involved heating or cooling the air, flowing at a known mass rate and in the reactor coil and recording the steady-state temperatures at the reactor

1 Durno and Hantho, CPE 83 Report, University of Alberta, 1953

"Heat Transfer from gases within a coil to a surrounding Bath"

entrance and at six ft.intervals. An overall coefficient
was calculated from a heat balance over the appropriate
sections and use of the modified Fourier equation

$$Q = U.A.\triangle T_{L.M.}$$

By using equations corelating heat transfer coefficients and
developed by other investigators, a value for the gas film
coefficient was estimated. Knowing the overall and gas film
coefficients, the bath film coefficient was calculated using the
series resistance to heat transfer concept.

Temperature corrections.

The inlet thermocouple well, No. 2, was inserted
co-axially within the reactor. From a steady state energy
balance across a unit well surface area, neglecting conduction
along the well because of its length, the following equation
results:

$$t_G - t_c = \frac{h_r \epsilon}{h_c} (t_c - t_w)$$

Values of h_r can be estimated from a chart[2] relating simplified
radiation coefficients to surface temperatures. The convective
heat transfer coefficient, h_c, may be estimated from the Dittus-
Boelter equation applicable to the heating or cooling of average
gases at turbulent conditions and the use of an equivalent
diameter , D_e,

$$\frac{h\,De}{k} = 0.023 \left(\frac{De\ G}{\mu}\right)^{0.8} \left(\frac{Cp\mu}{k}\right)^{0.4}$$

The value of h_c obtained was assumed applicable to both surfaces

2 McAdams, "Heat Transmission", Mc Graw-Hill, 1942, p.63

of the annular space. For well No. 2.

$$D_1 = 0.25 \text{ in.}$$

$$D_2 = 0.364 \text{ in.} \qquad , \quad D_e = D_2 - D1 = \frac{0.114}{12} \text{ ft.}$$

and $\quad G = \dfrac{W}{A} = \dfrac{W \ (144) \ 4}{\pi ((0.364)2 - (0.25)2)} = 2620 \ W \text{ lb/(hr.)(sq.ft.)}$

$$k = 0.0295 \quad \text{BTU/(hr.)(sq.ft.)(}^\circ\text{F per foot)}$$

$$\mu = 0.031 \ (2.42) \quad \text{lb/(sec.)(ft.)}$$

$$C_p = 0.26 \quad \text{BTU/(lb)(}^\circ\text{F)}$$

Substitution of the values for D_e and G, the average properties of air at a temperature of 750°F, in consistent dimensions, reduced the equation to the form

$$h_c = 6.30 \quad W^{0.8}$$

Corrections applied to thermocouple No. 3, 6 ft. from thermocouple No. 2, were obtained from the other temperature correction derivation, shown in the appendix, for a well placed normal to the direction of flow and corrected for radiation and conduction.

Calculation of film coefficients

The gas film heat transfer coefficient for the reactor was calculated by two methods, the average of which being used.

a. Dittus - Boelter equation applicable to highly turbulent fluids in a straight pipe

$$\frac{hD}{k} = 0.023 \quad \left(\frac{C_p \mu}{k}\right)^{0.4} \left(\frac{D \ G}{\mu}\right)^{0.8}$$

b. Jeschke equation for the cooling of air in

helical coils at turbulent flow up to Reynolds No of 150,000

$$\frac{hD}{k} = \left(0.039 + 0.138 \frac{D}{D_H} \right) \left(\frac{D \, G \, C_p}{k} \right)^{0.76}$$

Average values for the properties of air were used in the above

equations.

Recalculation of the experimental data is shown in the

attached table:

	Cooling air			Heating air		
Run No.	4-1	4-2	4-3	5-1	5-2	5-3
W lb/hr.	4.08	8.16	12.24	4.045	8.090	12.135
t_{c2} °F	877	906	871	377	351	310
t_{c3} °F	695	701	707	704	695	684
t_b °F	692	691	692	708	707.5	706
For thermocouple well No.2.						
t_w°F (est. using hároclor) $\doteq$25)	794	838	827	544	483	429
$h_c = 6.30$ $W^{0.8}$	19.5	34.0	46.7	19.2	33.3	45.2
$h_r\epsilon$	13.5	14.4	13.5	8	7.5	7
t_{G2} (corrected)°F	935	935	884	307	321	291
For thermocouple No.3:						
h_c (at wall-average of D.B. & Jes. Eg'ns)	10.3	18.6	25.3	10.2	17.5	24.0
t_w °F (est. using harodor $\doteq$25)	693	695	699	706.5	702	692
$h_r\epsilon$	11	11	11	10	10	10
h_c (for thermo-couple well)	70.5	107	136	70.1	106	135
Cosh ml	3.93	5.5	7.1	3.60	5.31	6.91
t_G3 (corrected°F)	696	703	709	702.2	692	681
To obtain coefficients:						
$\Delta T_1 - F°$	243	244	192	401	386.5	415
$\Delta T_2 - F^\theta$	4	12	17	5.8	15.5	25
$\Delta T_{L.M.}$	58.3	77.0	72.4	99.1	116	139
Temp. drop of gas $- F°$	239	232	175	395	371	396
$\dfrac{W\ Cp}{Ai}$	1.882	3.76	5.65	1.86	3.72	5.58

	Cooling air			Heating air		
Run No.						
$U = \dfrac{WCp}{Ai}\dfrac{(t_{G2}-t_{G3})}{T_{LM}}$	7.7	10.9	13.7	7.80	11.9	15.7
h_c (gas film coeff)	10.8	18.6	25.3	10.2	17.5	24.0
h_a (bath film coeff)	27.3	26.0	29.9	33.2	37.2	45.4

The calculated bath coefficients were found to be of
the order 27 to 45 BTU/(hr.)(sq.ft)(°F) being slightly lower
when the air was being cooled. As calculated, they show a
slight increase with increasing mass flow rate.

Use of the Jeschke and Dittus - Boelter equations
for determining an air film coefficient may introduce some
error but no other alternative was available. The pressure
drop in a coil due to fluid friction is greater than for a
straight pipe of equal diameter because of the added turbulence.
As would be expected the heat transfer coefficient then should
be greater for the coil. The Jeschke equation shows increased
values of h compared to those obtained with the Dittus-Boelter
equation which perhaps represents a minimum value for the air
film coefficient. Because the Jeschke equation was based upon
data which ranged up to DG/U of 150,000 and the actual reactor
conditions only reached a calculated value of DG/U of 8-10,000,
an average of the two calculated air film coefficients was chosen as a
closer approximation of the true value.

The transitional flow region boundaries applicable to
flow in the coil are not established and at the low flow rates,
the calculated coefficients may be too high.

The data obtained by Durno and Hantho may yet be subject
to error. From the study of the reaction temperature profiles,
corrected gas temperatures which are considerably greater than the

bath temperature are believed to be still low. As a result
the overall and the bath film coefficients may be too large.
The measurement of flow rates was not subject to error because
the displacement meter was accurately calibrated and the use of
air provides a fluid whose properties are well known.

The important factors to be considered in the reactor
heat transfer stem from the facts that neither gas nor bath film
are controlling and that the use of low flow rates may cause
overlap into the transitional flow region.

Thermocouple Corrections.

The reactor coil contained three thermocouple wells
which were placed normal to the flow of the gases. Because the
well surfaces in contact with the gases were very small and one
end of the well was attached to a surface cooler then the gases,
errors in temperature measurement were suspected. An attempt was
made to correct the recorded thermocouple temperature for error
introduced through heat losses by conduction and radiation.

Consider a small section of the well illustrated in the
diagram:
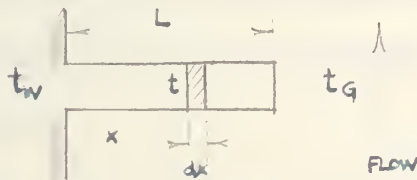
Perimeter of well   - P ft.

Cross-sectional area of well (metal only) - A sq.ft.

Thermal conductitivity of well metal   - k BTU/(hr.)(ft.)(°F)

Temperature of wall   - t_w °R

Temperature of well at distance X from wall - t °R

Temperature of well at distance L from wall - t_c °R

Total length of well - L ft.

Heat transfer coefficient, gas to well - h_c BTU/(hr.)(sq.ft.)(°F)

Emissivity - ϵ

Neglecting the heat introduced in the additional surface on the tip
of the well and radial thermal gradients in the well, a heat balance
over the differential section of length, dx, (defining heat in as
positive) shows

$$k A \frac{d^2t}{dx^2} \cdot dx + h_c P \cdot dx \ (t_G - t)$$
$$+ 0.173 \epsilon P \cdot dx \ \left\{ \left(\frac{t_W}{100}\right)^4 - \left(\frac{t}{100}\right)^4 \right\} = 0 \ \ldots(1)$$

The use of absolute temperatures to the fourth power may be eliminated by introducing a "radiation coefficient of heat transfer", i.e. $Q_r = h_r \epsilon A \ (t_W - t)$

The integration of equation (1) poses certain practical difficulties but if h_r is relatively small, an average value may be used without introducing too large an error. The value of h_c is based on the bulk properties of the flowing gases and is assumed constant over the total surface. Equation (1) then appears in the form

$$kA \ \frac{d^2t}{dx^2} = h_c P \ (t - t_G) + h_r \epsilon P \ (t - t_W)$$
$$" \quad = (h_c + h_r \epsilon) P t - (h_c P t_G + h_r \epsilon P t_W) \ \ldots(2)$$

and
$$\frac{d^2t}{dx^2} = \frac{P}{kA} \ (h_c + h_r \epsilon) \left\{ t - \frac{h_c t_G \ h_r \epsilon t_W}{h_c + h_r \epsilon} \right\} \ldots(3)$$

Equation (3) is of the form

$$\frac{d^2\theta}{dx^2} = M^2 \theta$$

where $\theta = t - \dfrac{h_c t_G + h_r \epsilon t_W}{h_c + h_r \epsilon}$

and $m = \sqrt{(h_c + h_r \epsilon) \ \dfrac{P}{kA}}$

and is identical to the one described in standard textbooks for heat transfer by conduction and convection only. The particular solution of this homogeneous differential equation for the point $X = L$, is given as:

$$\text{Cosh ml} \quad = \quad \frac{\theta t = t_W}{\theta t = t_c}$$

or $$\text{Cosh} \quad \overline{(h_c + h_r \in) \frac{P}{kA}} \cdot L = \frac{t_W - \frac{h_c t_G + h_r \in t_W}{h_c + h_r \in}}{t_c - \frac{h_c t_G + h_r \in t_W}{h_c + h_r \in}} \quad \cdots \cdots (5)$$

and after simplifying

$$t_G = \frac{\left[\frac{h_r}{h_c} \in (t_c - t_W) + t_c\right] \text{Cosh} \quad \text{ml} - t_W}{\text{Cosh} \quad \text{ml} - 1} \quad \cdots \cdots \cdots (6)$$

The application of this equation has been indicated earlier, but

in the equation shown for calculating h_c, the mass velocity was based

on the restricted passage between the tube and the tip of the well.

Aroclor Characteristics

Experience in the use of Aroclor indicated that continued use of this fluid at its boiling point led to its persistent decomposition. This breakdown changed its appearance from a clear syrup-like fluid at room temperature to a black amorphous solid. Corrosive decomposition products included hydrochloric acid. The boiling point was found to increase steadily, ranging from 680°F to 760°F after which the Aroclor was discarded.

To obtain a constant bath boiling point of approximately 725°F for all runs, it was necessary to boil the Aroclor under pressures ranging from 44 to 22 inches of mercury.

Process Operational Procedure

Preliminary

   1. Turn on cooling water to reactor bath condenser.

   2. Switch on reactor overload and transformer heating circuits and adjust transformer to high setting for initial heating.

   3. Switch on CuO furnace heater in offgas continuous sampler. To give temperature of 400°C. disconnect furnace tube inlet line and connect outlet to vacuum source. Switch on vacuum pump and draw slow flow of air through catalyst bed for re-oxidation.

   4. Switch butane preheater on when reactor bath temperature reaches 500°F. and start water flow through preheater bath condenser.

   5. Switch on N_2-O_2 preheater. Start air flow though N_2-O_2 preheater to prevent overheating.

   6. Switch on variable input heat tracing circuit so that insulation will attain temperature equilibrium with surroundings.

   7. Adjust air flow rate to corresponding desired rate of N_2-O_2 for run by checking offgas meter flow rate.

   8. Start cooling water through offgas cooler.

   9. Switch on Brown Temperature recorder.

   10. Check calibrated butane reservoir gauge to ensure that sufficient butane is present for duration of run, otherwise fill from butane reservoir.

   11. Check to make sure that 2 product bottles, gas sampling train, and Orsat are prepared.

   12. Shut vacuum pump off. Adjust CuO oxidation furnace transformer to give furnace temperature of 700°C.

   13. Reduce reactor heat input when bath temperature reaches boiling point. Control with transformer alone if possible.

   14. Start water flow into absorption tower and flood tower to wet the packing.

   15. Adjust N_2-O_2 preheater and heat tracing to control feed termperature at bath temperature.

   16. Turn on quench water to reduce offgas temperature to below 200°F.

17. Shut off air flow and close isolation valve.

18. Open N_2-O_2 cylinder valves and start N_2-O_2 flow through rotameter at desired rate.

19. Close valve on bypass line from ice-pot to tower.

20. Check reactor pressure gauge. Make necessary adjustments on reaction pressure reducing valve.

21. Start butane flow from main reservoir at desired rate.

22. Re-adjust N_2-O_2 preheater and heat-tracing, if necessary, so that gases enter reactor at bath temperature.

23. Change butane source to calibrated reservoir.

Before starting the measured time run, all of the following conditions must be satisfactory:

a) The reactor reaction time may be estimated by measuring the rate of passage of offgases through the offgas meter with a stopwatch and correcting this flow back to reactor conditions.

b) The CuO oxidation furnace must be at 700°C.

c) The offgas gas sample line should be purged up to the sample train and the sample train should be ready.

d) The composite gas sample collector should be ready.

e) The absorption tower should be drained of excess liquor and water introduced should be adjusted to give satisfactory scrubbing.

f) The ice-pot should be drained through the bypass valve.

g) Butane from the calibrated reservoir must be flowing and the level visible on the depth scale.

h) Sample bottles for product should be installed at tower liquid outlet.

i) Reaction should be evident by temperature chart.

j) Butane flow-rate should be checked over a 5-minute period by observing reservoir gauge depth change.

Operation

1. Measure volume on wet test meter with no flow but adjust to operating vacuum.

2. Start tower liquid product draining into waste liquid bottle.

3. Measure reading of offgas meter, butane reservoir level and start stopwatch.

4. Switch tower drain to sample collection bottle.

5. Start composite gas sampler.

6. Start gas flow through CuO oxidation furnace at slow rate to ensure complete oxidation. Note wet test meter pressure and temperature.

7. Take offgas sample and analyse with Orsat every 15-20 minutes.

8. Maintain constant flows with butane and N_2-O_2 rotameters (also H_2O if being measured into process.) Adjust N_2-O_2 rotameter if the offgas meter rate is found to be changing.

9. Adjust heaters if necessary to maintain steady state. Measure instantaneous temperatures of reactor feed with potentiometer.

10. Operate at desired conditions until sufficient product and data collected.

Shutdown

1. Drain tower and ice-pot into product bottle.

2. Measure butane reservoir, and offgas meter at same instant stopwatch closed.

3. Shut off composite gas sampler.

4. Leave gas train vacuum pump on but isolate sample line upstream of samplers, measure volume and switch to N_2 purge.

5. Shut down process equipment only when all samples are satisfactory.

6. Turn off all electrical switches including butane preheater.

7. Stop butane flow by closing isolation valve at base of preheater, then control valve and finally, isolation valve at reservoir:

8. Stop N_2-O_2 flow, close cylinder valves.

9. Shut off quench water.

10. Leave all condensers on until Aroclor baths are cooled.

-A43-

11. When sample train has been purged with N_2 shut off vacuum pump and remove bubblers. Note that sample bottles must be removed in proper sequence to prevent siphoning with consequent reagent mixing.

12. Analyze CO_2 samples by titration.

13. Analyze composite gas sample with Orsat.

14. Complete calculations as per outline.